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GRIC
2023

2nd Panhellenic Workshop on Inorganic Chemistry

Program & Book of Abstract

Amphitheater 'K. Karatheodori', National and Kapodistrian University of Athens

September 28-30, 2023

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A welcome to Chemistry Department of *NKUA* and GRIC-2023.

On behalf of the Scientific and Organizing committees, we are delighted to welcome you to Athens for the "2nd Panhellenic Workshop on Inorganic Chemistry (GRIC-2023)." This meeting is the second one of its kind, and it is an effort to bring together all active Inorganic Chemistry faculty members and researchers from Universities and Institutes in Greece and Cyprus to present, discuss, and share their research programs, emerging ideas, and scientific activities. The goal is to establish new collaborations, synergies, and consortiums for joint research funding.

The workshop will take place at the Amphitheater “K Karatheodoris” in Panepistimiopolis, Zografou, from September 28-30, 2023. It is co-organized by the Chemistry Department, Inorganic Lab, of the National and Kapodistrian University of Athens, and the Institute of Nanoscience and Nanotechnology of NCRS 'Demokritos.'

We hope that this conference will be highly active and serve as a forum for the exchange of the latest knowledge concerning inorganic chemistry and its disciplines among researchers. We anticipate fruitful discussions on the latest topics during several invited lectures and poster presentations.

The organizing committee gratefully acknowledges the financial support of our sponsors and the participation of all those contributing to the success of the Workshop. We look forward to welcoming you to Athens and wish that GRIC-2023 will serve as an inspiration to the next generation of scientists.

Christiana Mitsopoulou and Vassilis Psycharis

Co-Chairs of GRIC-2023.

Sponsors

We thank the following sponsors for their support to our Workshop.

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General Information

The 2nd Panhellenic Workshop on Inorganic Chemistry has no registration fees neither for the invited speakers nor the invited attendants. The registration of all invited speakers is mandatory, and this will include

Course Kit (bag) and name badge

Book of Abstracts

Sponsors' material

Certificate of Attendance

Official Dinner

The official dinner will take place on Thursday, September 28 at 20.30 (restaurant: The Egg of the Rooster, Metaxourgeio Athens)

Meeting and Event Program GRIC-2023

Thursday, September 28, 2023

9.00-10.00	Registration
10.00-10.30	Opening of the Workshop Welcome and Introductions • Professor Nikolaos Thomaidis, Member of the Council NKUA • Professor Evi Lianidou, Chair of Department of Chemistry, NKUA • Professor Christiana Mitsopoulou, Director of Inorganic Lab.. Chemistry Dept., NKUA and the Research Institute "Energy-Renewable Sources and Trasportations", Center of Research and Innovation, NKUA
	Chair : V. Psycharis
10.30-11.00	**S. Perlepes** *Our Recent "Adventures" in the Chemistry of Lanthanoids (4f) and Actinoids (5f)*
11.00-11.30	**C. Stamatatos** *Organic chelates vs nitrates… Peripheral site modification in a family of dinuclear single-molecule magnets bearing a* $\{Dy_2(\mu\text{-}OR)_2\}^{4+}$ *core and exhibiting dissimilar magnetic dynamics*
11.30-12.00	**M. Louloudi** *Plasmonic Nanoparticles (PNPs) in Molecular Catalysis*
12.00-12.30	Coffee Break
	Chair : C. Stamatatos
12.30-13.00	**A. Kanaras** *Synthesis, Surface Functionalization and Applications of Inorganic Nanoparticles*
13.00-13.30	**A. Salifoglou** *Vanadium in cell differentiation linked to metabolic syndromes*
13.30-14.00	**A. Keramidas** *Design and Modulation of Selectivity Towards Vanadium(V) and Uranium(VI) Ions: Coordination Properties and Affinity of Hydroxylamino-Triazine Siderophores*
14.00-16.00	Lunch –Poster presentation

	Chair : A. Kanaras
16.00-16.20	**V. Psycharis** *Structure relations in non-molecular crystal structures based on cation arrangement*
16.20-16.40	**K. Ladomenou** *Porphyrin-based complexes for efficient light-driven H2 evolution*
16.40-17.00	**K. Raptopoulou** Iron(III) complexes with polydentate ligands: Synthesis, structural, magnetic and spectroscopic characterization
17.00-17.20	**P. Kyritsis** *Zero-Field Splitting and Slow Magnetization Relaxation in Mononuclear 3d-Metal Complexes*
17.20-17.40	**P. Paraskevopoulou** *Polyurea-crosslinked alginate aerogels – design and synthesis of novel nanostructured materials with diverse applications*
17.40-18.00	**C. Methenitis** *Synthesis and characterization of Ag(0) nanoparticles stabilized in aqueous solution by L-amino acid derivative polyelectrolyte. In vitro evaluation of their cytotoxicity*
20.30	Official Dinner

Friday, September 29, 2023

	Chair : M. Louloudi
9.30-10.00	**S. Hatzikakou** *Organometallic compounds as targeted chemotherapeutics against adenocarcinoma cells*
10.00-10.20	**M. Chrysina** *Nature of S-States in the Oxygen-Evolving Complex Resolved by High-Resolution Fluorescence Detected X-ray Absorption Spectroscopy*
10.20-10.40	**C. Banti** *A novel metallo-antibiotic by Ciprofloxacin modification*
10.40-11.00	**G. Mitrikas** *Long Electron Spin Coherence Times of Atomic Hydrogen Trapped in POSS cages*
11.00-11.20	**M. Ziagkos**, Analytical Instruments A.E. *XRD has changed: Advancing Instrumental Methods of Analysis with Bruker's Groundbreaking XRD Technology*
11.20-12.00	Coffee Break

	Chair : K. Paptopoulou
12.00-12.20	**E. Efthimiadou** *Metal nanostructured materials for bioapplications*
12.20-12.40	**A. Garoufis** Cytotoxic activity of full-sandwich cycloparaphenylene(CPP)-Rucyclopentadienyl(Cp) polynuclear complexes
12.40-13.00	**N. Alexopoulos** *Investigation on the effect of artificial ageing kinetics on corrosion susceptibility of Al-Cu-Li 2198 alloy*
13.00-13.20	**A. Chrissanthopoulos** *Structural and vibrational properties' study of Arsenic Sulfide chemical species*
13.20-13.40	**A. Danopoulos** *Pincer' Complexes with N-Heterocyclic Carbene and Related Donors*
13.40-16.00	Lunch –Poster presentation
	Chair : T. Keramidas
16.00-16.30	**Y. Sanakis** *The Spin Relaxation Properties of Some Mononuclear S=2, Fe(II) Complexes.*
16.30-17.00	**G Malandrinos** *Coordination properties of Cu(II) ions towards peptide fragments located at the microtubule-binding domain of the longest tau isoform*
17.00-17.30	**G. Mousdis** *Low-Dimensional Organic-Inorganic Hybrid*
17.30-18.00	**A. Philippopoulos** *η 6 -Arene Ru(II) Complexes as Efficient Catalysts for Transfer Hydrogenation of Aromatic Ketones*
18.00-18.30	**N. Tsoureas** *Manipulating arene interactions in 1st row transition phenoxide metal complexes.*
	Closing Remarks- Announcement of GRIC 2025

Saturday, September 30, 2023

9.30-12.00	**Round Table**

ABSTRACTS

ORAL PRESENTATIONS

Our Recent “Adventures” in the Chemistry of Lanthanoids (4f) and Actinoids (5f)

S. T. Tsantis,[a,c] M. Iliopoulou,[a] Demetrios I. Tzimopoulos[b] and S. P. Perlepes*[a,c]

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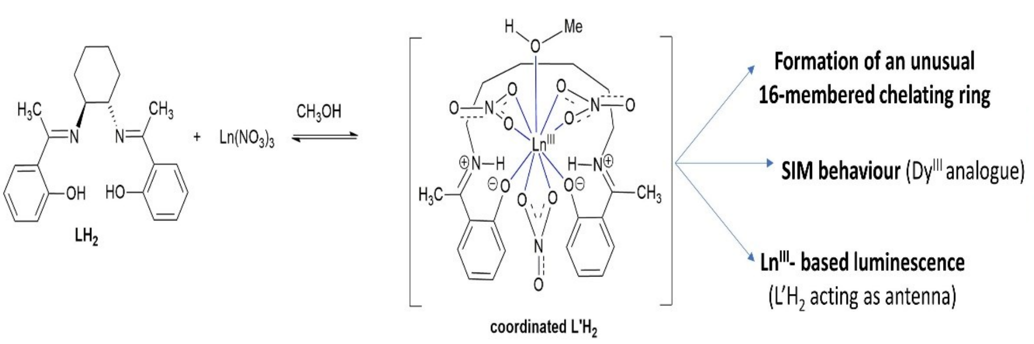
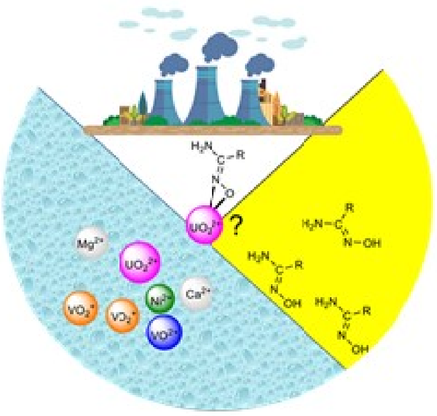
Inorganic Chemistry was dominated by transition metals (3d, 4d, 5d) in the second half of the 20th century [1]. In the last 20 years or so, there has been a considerable shift of focus on the chemistry of f metals. The 4f and 5f elements exhibit pronounced chemical similarities as two groups at the bottom of the Periodic Table, but simultaneously they express distinctive and varied electronic properties within each group. These atomistic properties are very useful and are the basis for applications in many technological properties, exploiting –between others- their magnetic, optical and catalytic properties. In our talk we shall try to focus on some “myths and truths” in the chemistry of 4f and 5f metals, and present some of our recent results in the chemistry of lanthanoids and actinoids. The latter involve (a) the synthesis and characterization of 4f-metal ion complexes with interesting properties, (b) the study of lanthanoid-promoted/assisted reactivity of coordinated ligands, and (c) the investigation of the synthetic and structural chemistry of uranyl-amidoxime complexes with emphasis on their technological implicaions.





[1] J. Ribas, Gispert, *Coordination Chemistry*, Wiley-VCH, Weinheim Germany, **2008**, pp. XXIV-XXXVII.

Organic chelates *vs* nitrates… Peripheral site modification in a family of dinuclear single-molecule magnets bearing a $\{Dy_2(\mu\text{-}OR)_2\}^{4+}$ core and exhibiting dissimilar magnetic dynamics

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The first use of the organic chelate *N*-hydroxy-1,8-naphthalimide (hynadH) in Dy^{III} chemistry has unveiled the access to a synthetic 'playground' composed of four new dinuclear complexes [1], all of which possess the same planar $\{Dy_2(\mu\text{-}OR)_2\}^{4+}$ diamond-shaped core, resulting from the bridging and chelating capacity of the hynad$^-$ groups. The structural stability of the central $\{Dy_2\}$ core has allowed us to modulate the peripheral coordination sites of the metal ions, and specifically the NO_3^-/hynad$^-$ ratio of capping groups, thus affording the compounds $[Dy_2(hynad)_2(NO_3)_4(DMF)_2]$ (**1**), $(Me_4N)_2[Dy_2(hynad)_2(NO_3)_6]$ (**2**), $[Dy_2(hynad)_4(NO_3)_2(H_2O)_2]$ (**3**), and $[Dy_2(hynad)_6(H_2O)_2]$ (**4**) in very good yields. Because of the chemical and structural modifications within **1**-**4**, the Dy^{III} coordination polyhedra are also dissimilar, comprising the muffin (**1** and **3**), tetradecahedral (**2**) and spherical tricapped trigonal prismatic (**4**) geometries. All compounds exhibit entirely visible out-of-phase (χ_M'') *ac* signals as a function of frequency and temperature, thus behaving as single-molecule magnets (SMMs), in the absence or presence of applied *dc* fields. Interestingly, the hynad$^-$-rich and nitrato-free complex **4**, demonstrates the largest - among all the other siblings- energy barrier (U_{eff} = 69.92 K) for the magnetization reversal (**Figure 1**), very likely due to the decoration of the two axial triangular faces of the spherical tricapped trigonal prism by the negatively charged O-atoms of the hynad$^-$ ligands [2]. The reported results may pave the way for the employment of *N*-hydroxyimides for the deliberate synthesis of dinuclear Ln-SMMs with interesting magnetic dynamics.

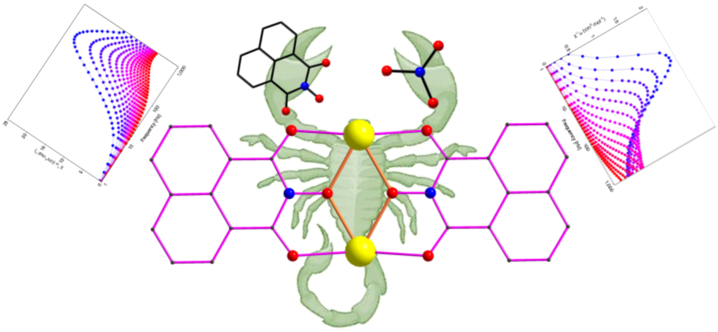

Figure 1. Structure-magnetism relationship in the reported family of $\{Dy_2\}$ SMMs.

[1] Habib, F.; Murugesu, M. *Chem. Soc. Rev.* **2013**, *42*, 3278−3288.

[2] Armenis, A. S.; Bakali, G. P.; Brantley, C. L.; Raptopoulou, C. P.; Psycharis, V.; Cunha-Silva, L.; Christou, G.; Stamatatos, Th. C. *Dalton Trans.* **2022**, *51*, 18077–18089.

Plasmonic Nanoparticles (PNPs) in Molecular Catalysis

Aikaterini Gemenetzi, Maria Louloudi*

Chemistry Department, University of Ioannina, Ioannina 45110, Greece
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Plasmonic nanoparticles (PNPs) present an interesting category of photo-active materials being able to harvest light energy by interacting with it through the excitation of localized surface plasmon resonance (LSPR). They have been used in catalysis as highly efficient enhancers, but not in molecular catalysis with well-known and functional systems.

We have studied two molecular catalytic systems in the presence of silver nanoparticles coated with silica. The first one, is a well-characterized LMn^{II} complex which catalyzes alkene epoxidation with H_2O_2 as oxidant. In this case, we demonstrated a concept where plasmonic nanoparticles can reversibly switch-off the catalytic oxidation process under light-excitation.[1] The second system is a very known Fe^{II} catalyst with a polyphosphine ligand which decomposes formic acid towards H_2-producction. We have recently shown that photoexcited core-shell $Ag^0@SiO_2$ plasmonic nanoparticles can dramatically enhanced the formic acid dehydrogenation (FADH).[2] In both cases we suggest the generation of hot electrons by the PNPs which either they are implicated in the reversible switch-off of the oxidation catalysis or boost H_2 production via FADH (Fig.1).[1,2] We consider that the phenomenon studied and published recently could be valid for many other metal-based molecular catalysts.

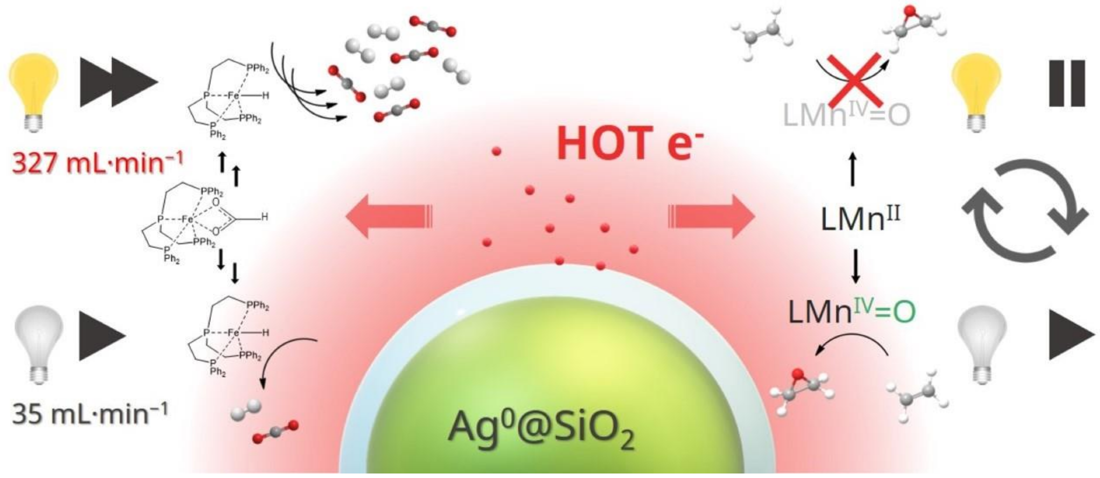

Figure 1. Plasmonic Nanoparticles in metal-based molecular catalysis[1,2]

[1] A.Gemenetzi, C.Moularas, L.Belles, Y.Deligiannakis, M.Louloudi, *ACS Catal*, **2022**, *12*, 9908.
[2] A.Gemenetzi, Y.Deligiannakis, M.Louloudi, *ACS Catal*, **2023**, *13*, 9905.

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Synthesis, Surface Functionalization and Applications of Inorganic Nanoparticles

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There is an enormous progress in the development of highly sophisticated nanoparticulate systems designed to perform multiple tasks in complex environments such as active layers of photovoltaic devices or complex biological environments. The properties of nanoparticles can be customized according to the choice of the chemical composition of the nanoparticle core, the morphology and the nature of nanoparticle surface chemistry. While an organic nanoparticle core can be sensitive in specific external stimuli such as pH, an inorganic core can provide nanoparticles with intrinsic optoelectronic, magnetic, catalytic and mechanical properties. Moreover, the choice of the ligands to coat the nanoparticle provides reactivity, targeted delivery and robustness in complex media.

In this presentation I will provide a brief overview of my research, concerning the design of nanoparticles and their utilization in biomedicine, diagnosis, energy and the environment. In more detail, I will discuss the customization of inorganic nanoparticles for applications in drug delivery, in DNA and mRNA sensing, in angiogenesis, in skin and as antimicrobial agents. I will also discuss the applications of nanoparticles in solar cells and LEDs as well as in catalysis.

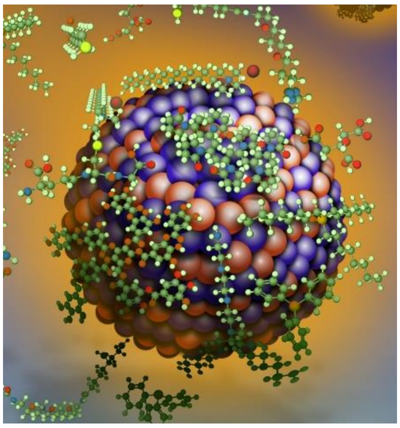

Figure. An artistic illustration of a nanoparticle functionalized with ligands.

[1] One or two references, if you wish: Heuer-Jungemann A. et al., *Chem. Rev.* **2019**, *119,* 4819-4880*.*

Acknowledgements: AGK would like to acknowledge funding from BBSRC, EPSRC, DSTL, Royal Society, the Leverhulme Trust and ATDBio.

Vanadium in cell differentiation linked to metabolic syndromes

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Metabolic syndromes have emerged as prevalent forms of aberrant physiologies in humans over the past century. Increasingly, humans of all ages have faced often undesired consequences of symptomatologies subdued to a plethora of metabolic syndromes, not the least of which include severe forms of diabetes, inevitably affecting their health and quality of life. The various drugs currently in the market target specified processes to ameliorate the symptoms and provide controllable approaches of therapeutic flavor. Unfortunately, however, all such drugs (e.g. metformin, sulfonylureas, meglitinides) exhibit side-effects and toxicity. Cognizant of such undesirable side-effects, we launched research efforts in our lab to develop metallodrugs that could a) possess atoxic biological behavior, b) bear no side-effects, mimic insulin or synergically enhance its activity in adipocytes, and c) target early events in metabolic diseases, such as Diabetes mellitus II. The effort was based on the rational design and pH-dependent synthesis of V(IV) and V(V) species bearing physiologically relevant organic substrates originating in the energy-producing machinery of adipocyte cells. The family of such metal-organic species were investigated in the solution and solid state, thereby providing a well-defined physicochemical profile. Based on such a profile, an extensive investigation ensued involving a) toxicity studies (cell viability, morphology, migration, proliferation), b) cell differentiating ability of fibroblasts, leading to mature adipocytes capable of initiating glucose uptake processes, and c) perusal of genetic machinery molecular targets (de)activated along the course of action, leading to mature adipocytes during cell differentiation [**1**]. The collective results, formulate the a) structural attributes of the vanadium-substrate complex species inducing cell differentiation of early stem cells, b) conditions under which molecular target chemistry enhances or stays quiescent in the presence/absence of insulin, providing an overall cohesive picture of a biological activity profile that justifies the bioinorganic role of vanadium in insulin mimesis and proffers merit for further development on fine-tuned vanadodrugs in Diabetes mellitus administration of biological events.

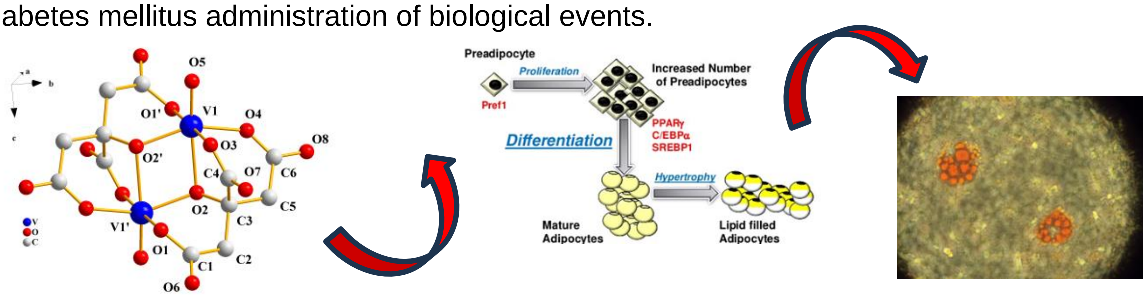

Figure 1. Schematic presentation of V(IV-citrate cell differentiation of fibroblasts.

[1] O. Tsave, A. Salifoglou, *J. Inorg. Biochem.*, **2021**, *214*, 111290

Design and Modulation of Selectivity Towards Vanadium(V) and Uranium(VI) Ions: Coordination Properties and Affinity of Hydroxylamino-Triazine Siderophores

Anastasios Keramidas[a], *Angelos Amoiridis,*[a] *Michael Papanikolaou,*[a] *Manolis Vlasiou,*[b]
Nuno A. G. Bandeira,[c] *Haralampos N. Miras,*[d] *Themistoklis Kabanos*[e] *

[a] *University of Cyprus,* [b] University *of Nicosia,* [c] *Universidade de Lisboa,* [d] *The University of Glasgow,* [e] *University of Ioannina*

Increase in energy demands by a constantly growing population combined with drastic geopolitical changes has driven the quest for energy sovereignty towards a variety of alternative forms one of them being the nuclear power. However, issues associated with waste management, environmental remediation, and recovery of radionucleotides has focused the efforts of researchers into developing systems appropriate for these applications. Siderophore ligands containing N,O hard donor atoms exert high affinity and selectivity for hard metal ions, including trans-$[U^{VI}O_2]^{2+}$ and cis-$[V^{V}O_2]^{+}$ which can render them excellent candidates in the extraction of hard metal ions from human body, radioactive waste, and seawater. A scientific challenge is the design of siderophores with improved coordination properties, thermodynamic stability and selectivity. Based on the strong binding and high selectivity properties of 2,6-bis[hydroxy(methyl)amino]-4-morpholino-1,3,5-triazine (H_2bihyat) for trans-$[U^{VI}O_2]^{2+}$, novel bi-nucleating ligands (BLs) N,N',N'',N'''-((1,4-phenylenebis(oxy))bis(1,3,5-triazine-6,2,4-triyl))tetrakis(N-methylhydroxylamine) (H_4qtn), N^1,N^4-bis(4,6-bis(hydroxy(methyl)amino)-1,3,5-triazin-2-yl)benzene-1,4-diamine (H_4pdl) and N^1,N^2-bis(4,6-bis(hydroxy(methyl)amino)-1,3,5-triazin-2-yl)ethane-1,2-diamine (H_4enl) were synthesized. Binuclear complexes formed by coordination of hard metal ions with H_4qtn are thermodynamically more stable than their mononuclear analogues with H_2bihyat, due to the increase in entropy accompanying the formation of more chelate rings. Reaction of either H_4qtn or H_4pdl or H_4enl with trans-$[U^{VI}O_2]^{2+}$ and cis-$[V^{V}O_2]^{+}$ resulted in the isolation of the binuclear complexes $[(U^{VI}O_2)_2(\mu\text{-qtn})(H_2O)_2]$ (**1**), $[(V^{V}O_2)_2(\mu\text{-qtn})]^{2-}$ (**2**), $[(U^{VI}O_2)_2(\mu\text{-pdl})(H_2O)_2]$ (**3**), $[(V^{V}O_2)_2(\mu\text{-pdl})]^{2-}$ (**4**), $[(U^{VI}O_2)_2(\mu\text{-enl})(H_2O)_2]$ (**5**) and $[(V^{V}O_2)_2(\mu\text{-enl})]^{2-}$ (**6**). The binuclear complexes **1** - **6** were characterized by single crystal X-ray diffraction analysis in solid state and by NMR and ESI-MS in solution. The comparison of the coordination ability of the BLs with either pyridine-2,6-dicarboxylic acid (H_2dipic) or H_2bihyat or CO_3^{2-} towards trans-$[U^{VI}O_2]^{2+}$ and cis-$[V^{V}O_2]^{+}$ was investigated by NMR and UV-vis spectroscopies and DFT theoretical calculations, revealing a superior performance of BLs. The selectivity of the BLs for trans-$[U^{VI}O_2]^{2+}$ over cis-$[V^{V}O_2]^{+}$ has been decreased compared with that of H_2bihyat but increases considerably at pH>9 values. Formation of the mixed metal binuclear species $\{U^{VI}O_2(\mu\text{-}O)V^{V}O_2\}$ influences the selectivity and the dynamics of the reaction of H_4qtn for trans-$[U^{VI}O_2]^{2+}$ and cis-$[V^{V}O_2]^{+}$ in aqueous solution. The results of this study provide crucial information for the ligand design the development of stronger and more selective systems.

ACKNOWLEDGMENTS

The research work was funded by the European Regional Development Fund and the Republic of Cyprus through the Research and Innovation Foundation (Project: EXCELLENCE/0421/0520).

Structure relations in non-molecular crystal structures based on cation arrangement

Vassilis Psycharis [1*], Manolis Chatzigeorgiou[2], Dimitris Niarchos[1], Michael Pissas[1].

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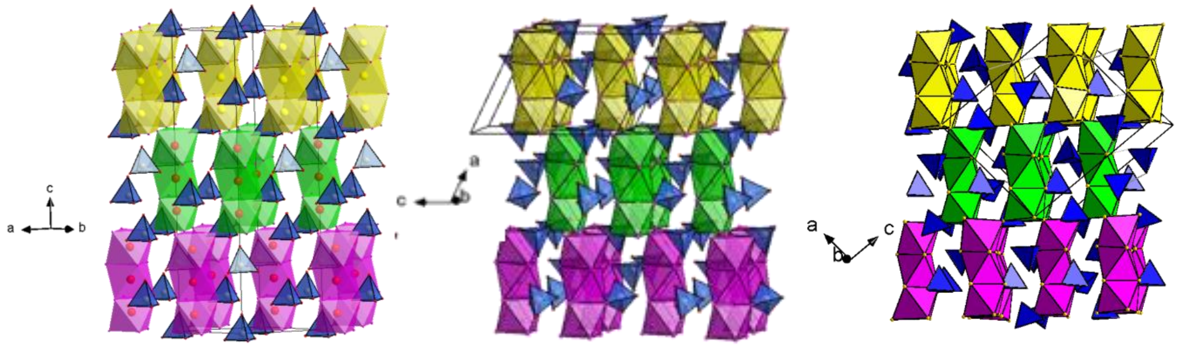
O'Keefe & Hyde [1a, 1b] use a description for non-molecular structures which is based on the arrangement of cations. This approach gives a simpler pattern for the arrangement of atoms in the structures and is an alternative to the usual description of polyhedra based on anions and introduced by Pauling [1]. Especially in the case of ternary oxides with two different metals the packing of cations resembles the packing of cations in alloys. In the present work the structure relations of the polymorphs of Alite,(tricalcium silicate, Ca_3SiO_5) the major cement phase (>70% exists in the clinker), will be discussed. The complications related to the various ways of structure description for the seven polymorphs of Alite have been discussed in the reference [3]. Our description uses the polyhedra formed by Ca^{2+}, which were discussed for first time in [3], and follow the ideas of O'Keefe & Hyde, give a clearer picture for the structures of Alite polymorphs and for the structure-relations as well. This description makes also clear the suggestion given in [5], that tricalcium silicate has to be considered as tricalcium oxy silicate. Within this context the recently claimed as RT superconductor lead apatite phase will be discussed.

Tricalcium Silicate polymorphs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[1] (a) O'Keeffe, M. & Hyde, B.G., 1985, 61, 77-144; b Vegas, Crystallography Reviews, 2000, 7, 189-283; (b) Vegas & A.; Mattesini, M., Acta Cryst. , 2010, B66, 338-344

[2] Pauling L. The Nature of the Chemical bond and the Structure of Molecules and Crystals: An Introduction tp Modern Structural Chemistry. 3rd Edition, New York Cornell University Press, Ithaka, USA, 1960; pp 505

[3] Dunstetter F., de Noirfontaine M.-N., Courtial M. *Cement and Concrete Research*. **2006**, *36(1)*, 39-53.

[4] Dent Glasser, Acta Cryst., 1965, 18, 455-457

[5] Plank J., Cement and Concrete Research. 2020, 130, 105957.

Porphyrin-based complexes for efficient light-driven H_2 evolution

Kalliopi Ladomenou* [a] Vasilis Nikolaou,[b] Eleni Agapaki,[b] Athanassios G. Coutsolelos[b,c]

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[b] *Laboratory of Bioinorganic Chemistry, Department of Chemistry, University of Crete, Voutes Campus, 70013 Heraklion, Crete, Greece.*
[c] *Institute of Electronic Structure and Laser (IESL) Foundation for Research and Technology - Hellas (FORTH), Vasilika Vouton, 70013 Heraklion, Crete, Greece.*
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Hydrogen is regarded a promising molecular fuel for clean energy production, capable of replacing fossil fuels and contributing to the resolution of global energy and environmental problems. Therefore, the efficient production of H_2 is of great significance, with the most promising strategy being the photocatalytic splitting of water.[1] In this study, dye-sensitized photocatalytic systems (DSPs) were developed by utilizing porphyrins as photosensitizes (PS) or as photosensitizer/catalyst entities (PS/CAT) upon their chemisorption onto platinum doped titanium dioxide nanoparticles (Pt-TiO_2 NPs). The DSPs coated with Pt-Tc3CP (PS/CAT entity) illustrated a record-high stability (25500 TONs) and H_2 evolution activity (707 mmol g^{-1} h^{-1}) with respect to similar systems mentioned in the literature.[2]

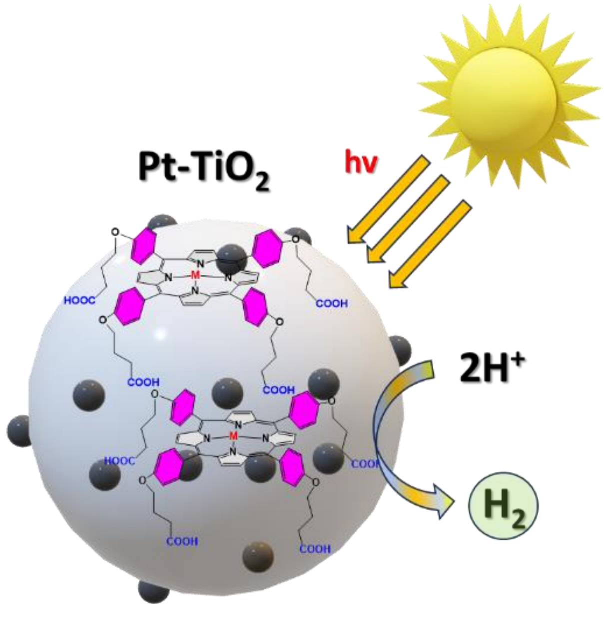

Figure 1: Design of dye-sensitized photocatalytic system for H_2 evolution reaction.

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Iron(III) complexes with polydentate ligands: Synthesis, structural, magnetic and spectroscopic characterization

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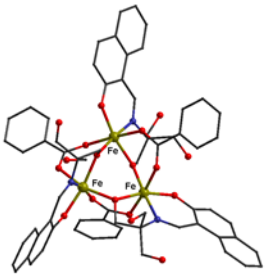
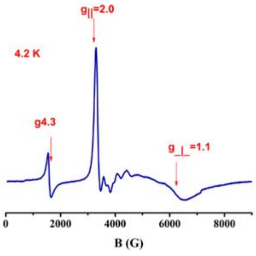
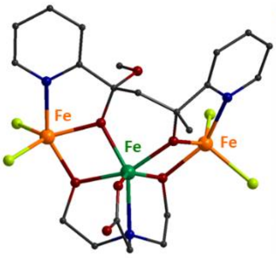
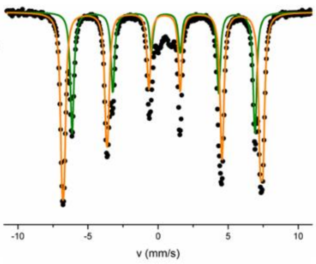
Organic ligands play a vital role in metal coordination chemistry which originates from the chemical nature and relative orientation of the donor atoms as well as their chelating and bridging ability. The complexation of an organic ligand around a metal ion affects its chemical properties, such as acidity, redox behavior, electrophilic or nucleophilic character etc. Usually, organic ligands and suitable inorganic/organic ligands are allowed to react with metal salts or metal precursors; however, the *in situ* formation of the organic ligands by simple and effective organic reactions is a commonly used method. Additionally, in some cases the organic ligands undergo chemical reactivity at specific active sites/groups upon coordination to metal ions, affording new organic molecules, with unprecedented structures, available for coordination to the metal ions. In many cases, the metal ions play probably a catalytic role in the *in situ* transformation of the organic precursor and the reaction is metal-ion assisted.

We will discuss the synthesis, structural, magnetic and spectroscopic characterization of iron(III) complexes containing ligands formed in situ, either by simple organic reactions, such as condensation reaction between aldehydes and amines leading to Schiff base ligands, or by more complicated organic reactions due to transformations of the organic precursors in the presence of metal ions.









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Zero-Field Splitting and Slow Magnetization Relaxation in Mononuclear 3d-Metal Complexes

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Ever after 2010,[1] a large number of mononuclear 3d-metal complexes have been shown to exhibit slow relaxation of magnetization, often associated with the presence of significant zero-field splitting (zfs).[2-3] Magnetometry and various spectroscopic techniques, such as high- frequency and -field EPR (HFEPR) and Far-IR Magnetic Spectroscopy (FIRMS), are methods of choice for the determination of the latter.[4] The coordination chemistry of the $\{R_2P(E)NP(E)R_2\}^-$ ligands (E = O, S, Se; R = alkyl or aryl group) towards transition metal elements has been shown to be rather versatile.[5] Specific examples of $S = 1$ tetrahedral Ni(II),[6] $S = 2$ octahedral Mn(III) [7] and tetrahedral Fe(II),[8] as well as $S = 3/2$ tetrahedral [9,10] and octahedral [11] Co(II) complexes bearing these ligands and exhibiting either large zfs or slow relaxation of magnetization will be discussed. In addition, spectroscopic, magnetic and electrocatalytic studies on novel $S = 3/2$ tetrahedral Co(II) complexes of the general type $\mathbf{Co}\boldsymbol{S}_\mathbf{2}\mathbf{Cl}_\mathbf{2}$, $\boldsymbol{S}$ = thiosemicarbazone ligand, will be presented. A similar $\mathbf{Co}\boldsymbol{S}_\mathbf{2}\mathbf{Cl}_\mathbf{2}$-type complex has recently been shown to be an electrocatalyst for the hydrogen evolution reaction (HER).[12]

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Polyurea-crosslinked alginate aerogels – design and synthesis of novel nanostructured materials with diverse applications

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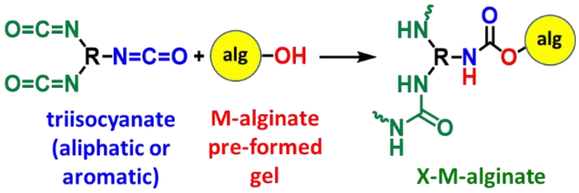
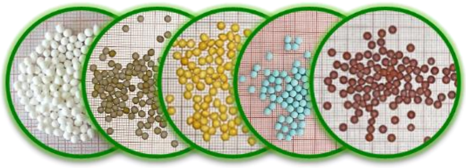
Alginate aerogels are very attractive materials because they: (a) come from renewable (natural) resources; (b) are prepared in water; (c) bear a large number of functional groups available for coordination to metal ions, hydrogen bonding, functionalization etc.; (d) are biocompatible, biodegradable and non-toxic; and, (e) can be converted pyrolytically to carbon aerogels with high open porosities and surface areas. However, their main drawbacks are that they are mechanically weak and extremely hydrophilic materials. These issues have been rectified with the introduction of polyurea-crosslinked alginate (X-M-alginate) aerogels [1-3].

In terms of their mechanical properties, X-M-alginate aerogels can be as stiff as the best organic aerogels at half or the one third of their density. They are also extremely stable in all aquatic environments (pH 2-9), including seawater and various wastewaters. These properties, along with their ability to bind different metal cations, have allowed applications to:
(a) environmental remediation, as adsorbents of heavy metals, organic solvents and dyes;
(b) biomedicine, as candidate materials for implants; and,
(c) the preparation of metal- and N-doped carbon aerogels in good yields, suitable for porous carbon electrodes and supercapacitors.





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Synthesis and characterization of Ag(0) nanoparticles stabilized in aqueous solution by L-amino acid derivative polyelectrolyte. *In vitro* evaluation of their cytotoxicity.

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Metallic nanoparticles have been of considerable scientific and technological interest because to their excellent properties and the wide range of applications [1–3]. Due to high surface to volume ratio, nanoparticles show high reactivity, so it is necessary to use capping agents as stabilizers that inhibit the over-growth of nanoparticles and prevent their aggregation/coagulation in colloidal synthesis [3-4]. In this regard, the water-soluble polymers, polyelectrolytes, that function as stabilizers of metallic nanoparticles have demonstrated to be excellent stabilizing agents of colloidal metallic nanoparticles [5-6]. In this context, we report the synthesis and characterization of silver nanoparticles, Ag(0), stabilized by the polyelectrolyte poly-N-methacryloyl-L-alanine (PNMA), as well as the in vitro evaluation of their biological activity. Potentiometric titrations, Ultraviolet-Visible absorption spectroscopy (UV-Vis) and Circular Dichroism (CD) spectroscopy were used to characterize Ag(I)-interaction. The characterization of Ag(0) stabilized by PNMA, the techniques of UV-Vis, Infrared Spectroscopy (IR), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), Transmission electron microscopy (TEM) and X-ray Diffraction (XRD) spectroscopies were used. Cytotoxicity of The Ag(0)-PNMA nanoparticles was studied by MTT method, in healthy HEK 239 cells.

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Organometallic compounds as targeted chemotherapeutics against adenocarcinoma cells

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The conjugation of organotin(IV) and organoantimony(III/V) moieties with natural products ingredients (NPI= carvacrol, acetic acid, salicylic acid, cholic acid) is reported [1]. The new formulations were characterized in solid state by melting point, X-ray Fluorescence (XRF), Attenuated Total Reflection Furrier Transform Infra-Red (ATR-FT-IR) spectroscopies, while UV-Vis and NMR spectroscopies were used for the characterization in solution.

The *in vitro* anti-proliferative activity of the new compounds were evaluated against human breast adenocarcinoma cancer cell lines: MCF-7 (positive to hormones receptor (HR+)), MDA-MB-231 (negative to hormones receptor (HR-)). The *in vitro* toxicity was checked against normal human fetal lung fibroblast cells (MRC-5). The *in vitro* genotoxicity was tested with the micronucleus (MN) assay using fluorescence microscopy. Moreover, *Artemia salina* assay and *Allium cepa* assays were used for the *in vivo* toxicity. The MCF-7 cells morphology suggests apoptotic pathway, especially through the mitochondrion damage, which was confirmed by DNA fragmentation, Acridine Orange/Ethidium Bromide (AO/EB) Staining and permeabilization of the mitochondrial membrane tests. Their binding affinity toward the calf thymus CT-DNA was *ex vivo* investigated by Uv-Vis, Fluorescence spectroscopies and viscosity measurements.

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Acknowledgments

This program is co-financed by Greece and the European Union (European Social Fund- ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning 2014-2020» in the context of the project “Sub-project 6 (“Biological Inorganic Chemistry (BIC)” (MIS 5162213).”

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Nature of S-States in the Oxygen-Evolving Complex Resolved by High-Resolution Fluorescence Detected X-ray Absorption Spectroscopy

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Photosystem II, the water splitting enzyme of photosynthesis, utilizes the energy of sunlight to drive the four-electron oxidation of water to dioxygen at the oxygen-evolving complex (OEC). The OEC harbors a Mn_4CaO_5 cluster that cycles through five oxidation states S_i (i = 0–4). The S_3 state is the last metastable state before O_2 evolution. Its electronic structure and the nature of the $S_2 \rightarrow S_3$ transition are key topics of persisting controversy. Most spectroscopic studies suggest that the S_3 state consists of four Mn(IV) ions, compared to the Mn(III)Mn(IV)$_3$ of the S_2 state. However, recent crystallographic data have received conflicting interpretations, suggesting either metal or ligand-based oxidation, the latter leading to an oxyl radical or a peroxo moiety in the S_3 state. Herein, we utilize high energy resolution fluorescence detected (HERFD) X-ray absorption spectroscopy to obtain a highly resolved description of the Mn pre-edge region for all S-states, paying special attention to use chemically unperturbed S_3 state samples. In combination with quantum chemical calculations, we achieve the assignment of specific spectroscopic features to geometric and electronic structures for all S-states. These data are used to confidently discriminate between the various suggestions concerning the electronic structure and the nature of oxidation events in all observable catalytic intermediates of the OEC. Our results do not support the presence of either peroxo or oxyl in the active configuration of the S_3 state. This establishes Mn-centered storage of oxidative equivalents in all observable catalytic transitions and constraining the onset of O–O bond formation until after the final light-driven oxidation event.

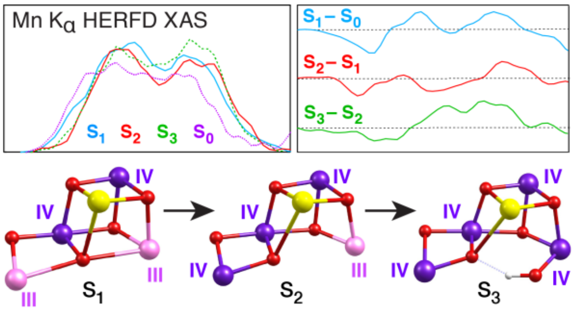

Figure. Mn Kα HERFD pre-edge of the S-states of the oxygen-evolving complex and the correlated DFT structures of the S_1, S_2 and S_3 states

Acknowledgements: The NCSR "Demokritos" (program E11143, "He liquefier and spectroscopy") and the Max-Planck Society (Max-Planck Partner Group program, "Study of the Photosynthetic Water splitting by Electron paramagnetic Resonance and X-ray Spectroscopy") are kindly acknowledged for the financial support.

A novel metallo-antibiotic by Ciprofloxacin modification

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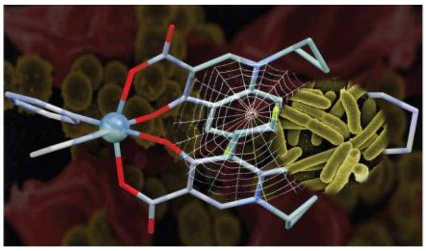
The synthesis of the metallo-antibiotic of formula $Ph_2Sn(CIP)_2$ (CIPTIN) (HCIP = ciprofloxacin) is reported [1]. The complex was characterized in the solid state by melting point, FT-IR, X-ray Powder Diffraction (XRPD) analysis, ^{119}Sn Mössbauer spectroscopy, X-ray Fluorescence (XRF) spectroscopy, and Thermogravimetry/Differential Thermal Analysis (TG-DTA) and in solution by UV-Vis, 1H NMR spectroscopic techniques and Electrospray Ionisation Mass Spectrometry (ESI-MS). The crystal structure of CIPTIN and its processor HCIP was also determined by X-ray crystallography [1].

The antibacterial activity of CIPTIN, HCIP·HCl, HCIP and DPTD was evaluated against the bacterial species *Pseudomonas aeruginosa (P. aeruginosa*), *Escherichia coli* (*E. coli*), *Staphylococcus aureus* (*S. aureus*) and *Staphylococcus epidermidis* (*S. epidermidis*), by the means of Minimum Inhibitory Concentration (MIC), Minimum Bactericidal Concentration (MBC) and Inhibition Zones (IZs). CIPTIN is classified into bactericidal agents. The developing IZs classify the microbes *P. aeruginosa, E. coli, S. aureus* and *S. epidermidis* to susceptible ones to CIPTIN. CIPTIN exhibits 2 to 9-fold lower MIC values than its IC_{50} against HaCaT, while its genotoxic effect determined by micronucleus assay is equivalent to the corresponding ones of HCIP·HCl or HCIP [1].



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Acknowledgments

This program is co-financed by Greece and the European Union (European Social Fund- ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning 2014-2020» in the context of the project "Sub-project 6 ("Biological Inorganic Chemistry (BIC)" (MIS 5162213)."

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Long Electron Spin Coherence Times of Atomic Hydrogen Trapped in POSS cages

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Encapsulated atomic hydrogen in octa-silsesquioxane (POSS) cages of the $Si_8O_{12}R_8$ type (where R is an organic group) is the simplest alternative stable system compared to the more expensive paramagnetic endohedral fullerenes ($N@C_{60}$ or $P@C_{60}$) that have been regarded as key elements in spin-based quantum technologies. Apart from common sources of decoherence like nuclear spin and spectral diffusion, all H@POSS species studied so far suffer from additional shortening of T_2 at low temperatures due to methyl group rotations [1]. Here I will discuss how we managed to eliminate this factor for the first time by studying the relaxation properties of the smallest methyl-free derivative of this family, namely $H@T_8H_8$. We suppress nuclear spin diffusion by applying dynamical decoupling methods and we measure the longest electron spin coherence time $T_2 = 280 \pm 76$ μs at $T = 90$ K observed to date for this family of materials. This unprecedented level of improvement paves the way for considering H@POSS as a distinguished qubit candidate for spin-based quantum computing, equally important to paramagnetic endohedral fullerenes.

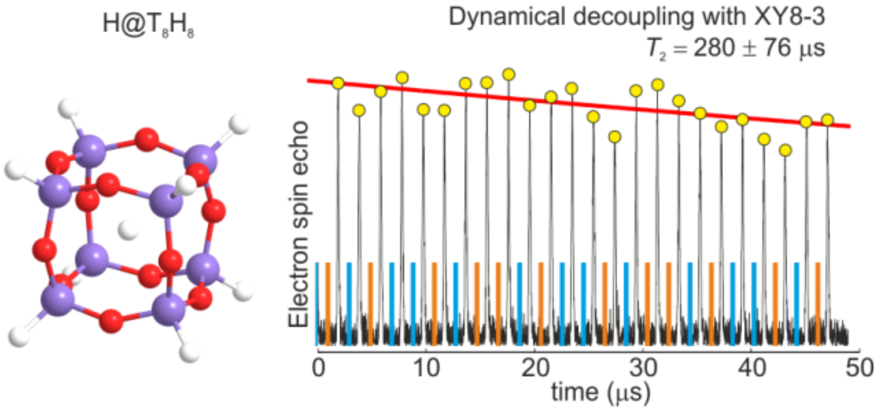

Figure. Structure of POSS molecule with R=H and decay of electron spin coherence

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XRD has changed: Advancing Instrumental Methods of Analysis with Bruker’s Groundbreaking XRD Technology

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For more than 60 years, Bruker has created innovative analytical instruments, to support the scientific community, as well as the users in Industry. Our analytical solutions stand for cutting edge technology and highest performance. While we are providing top technology for scientists worldwide, over the past decades, we have more and more focused, on making the latest analytical methods, also accessible to a broader group of users. At the forefront of this endeavor for accessibility are our benchtop instruments. Although they come with a smaller footprint than our landmark full sized systems, they share with them the same analytical instrument DNA, including the focus on data quality, robust hardware design and reliable results. Today we are happy to introduce a new member of our benchtop solution family, the D6 PHASER. The D6 PHASER is the base of a new world of X-Ray Diffraction solutions with compact size and unparalleled flexibility.

Metal nanostructured materials for bioapplications

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Noble metal nanostructured materials are an important part of nanotechnology which has shown a wide range of application like new energy storage systems, photocatalysis and bioapplications. This kind of materials combined the special physical and chemical properties of noble metals with nanomaterials to exhibit superior performance, expanding the application range of nanomaterials.

Methods and functional properties of various nano-structured materials of noble metals as well as their applications are presented in this work. Applications of typical noble metal nanomaterials with different properties for chemical and theranostic systems are also presented. In this work is presented the significance of functional properties of different metal nanomaterials and expand their applications in various research fields, especially in biomaterials.

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A second part of this work was co-financed by Greece and the European Union (European Social Fund – ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning 2014 – 2020» in the context of the project "Innovative Titanium Nanoparticles for Development of Autocleaning and Auto antibacterial Application" (MIS 5131364, TiClean).

Cytotoxic activity of full-sandwich *cyclo*paraphenylene(CPP)-Ru-cyclopentadienyl(Cp) polynuclear complexes

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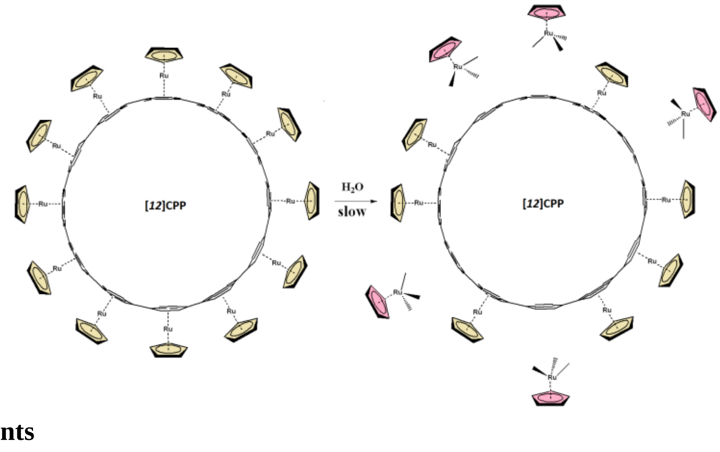
In recent years cycloparaphenylenes (CPP's) have garnered significant attention from scientists due to their unique photophysical, photochemical and physicochemical properties [1]. The synthesis of either classic or modified cycloparaphenylenes and the large number of their potential applications has opened up a new field of research in modern synthetic chemistry. CPP's may be modified by $\{RuCp\}^+$ units (Cp is the cyclopentadienyl anion) forming complexes of the general formula $[(CPP)(RuCp)_n]Cl_n$ [2]. In parallel, it is well established that ruthenium arene complexes exhibit high cytotoxicity *in vitro* and *in vivo* and a particular selectivity for cancer cells as well. Taking these factors into consideration, along with the high lipophilicity of CPPs and the solubility of these complexes, we proceeded on the synthesis, characterization, and comprehensive study of fully substituted [12]CPPs, where each phenylene unit was η^6-coordinated with $\{RuCp\}^+$ units, employing a full-sandwich mode (*see* figure). The complex $[([12]CPP)(RuCp)_{12}]^{12+}$, which was isolated as $[PF_6]^-$ salt and was stable in acetonitrile and acetonic solution for a period of time over 48 hours, was completely insoluble in aqueous media. However, its corresponding $[Cl]^-$ salt exhibited a good water solubility, gradually releasing the $\{RuCp\}^+$ units after 2 hours of dissolution. In contrast, the complexes with linear paraphenylenes, $[(LPP)(RuCp)_n]Cl_n$ (where n = 3-5) displayed remarkable stability in aqueous media and only released $\{RuCp\}^+$ moieties when it exposed to UV irradiation. The complex $[([12]CPP)(RuCp)_{12}]^{12+}$ showed cytotoxicity against the cell lines which was used, with IC_{50} values ranging in the scale of a few μM. Notably, the A2780 cisplatin-resistant cell line displayed the highest IC_{50} value of 4.76 μM. Importantly, the cytotoxic activity of the $\{RuCp\}^+$ unit, produced from the $[RuCp(CH_3CN)_3]PF_6$, exhibited higher IC_{50} values >200 μM. This information suggests that the cytotoxicity arises primarily from the main complex $[([12]CPP)(RuCp)_{12}]^{12+}$ or species such as $[[12](CPP)(RuCp)_n]^{n+}$, which may interact with biological targets, rather than from the $\{RuCp\}^+$ units themselves.



Acknowledgements

Konstantinos Ypsilantis was financially supported by the project "Center for Research, Quality Analysis of Cultural Heritage Materials and Communication of Science" (MIS 5047233) implemented under the Action "Reinforcement of the Research and Innovation Infrastructure", funded by the Operational Program "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).

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Investigation on the effect of artificial ageing kinetics on corrosion susceptibility of Al-Cu-Li 2198 alloy

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The increasing demand in the aviation industry for continuous improvement in energy efficiency along with mechanical performance and damage tolerance, led to the development of lighter metallic structures. Third generation Al-Cu-Li alloys were developed to replace the conventional Al-Cu aluminum alloys, since they can offer approximately 5 % weight reduction of the structure as well as improved property balance and corrosion resistance. Their improved mechanical properties are often attributed to their precipitation hardening system, including δ (Al_3Li), ϑ (Al_2Cu), T_1 (Al_2CuLi) and S (Al_2CuMg) second-phase precipitates. Nevertheless, these kinds of precipitates may influence the electrochemical behaviour of such alloys, due to the different electrochemical behaviour of the intermetallic phases and the matrix [1,2,3], and consequently increase corrosion susceptibility. The size and population of such intermetallic phases alters significantly during natural ageing of the aluminum structures. For the simulation of the natural ageing of the aluminum structures, usually artificial ageing heat-treatment is performed in order to accelerate the thermos-mechanical transformations that have an immediate impact on the metallurgical structure, on the residual stress state and finally on the mechanical properties. Alloys from the 2xxx aluminum alloy series, e.g., 2024, was found to have higher corrosion resistance when artificially aged at certain tempers, such as T6, than at T3 [4]. Hence, it is of major importance to investigate the effect of artificial ageing on corrosion behaviour on the third generation Al-Cu-Li alloys.

The material used was a wrought aluminum alloy 2198-T3 which was received in sheet form of 3.2 mm nominal thickness. Small rectangular specimens [10 mm x 20 mm] were machined from the sheets and then the specimens were exposed to artificial ageing heat-treatment for different ageing times; different ageing tempers were selected that corresponded to under-ageing (UA), peak-ageing (PA) and over-ageing (OA) tempers. Exposure of the specimens to 3.5 wt. % NaCl solution according to ASTM G44 specification was performed for different exposure times to investigate the effect of artificial ageing on the corrosion evolution. Electrochemical impedance spectroscopy as well as potentiodynamic polarization measurements were performed to identify the corrosion kinetics and simulate the corrosion-induced degradation mechanism. The results were correlated with the respective results from light optical microscopy investigations.

Artificial ageing was found to affect the corrosion kinetics and corrosion-induced degradation mechanism of the investigated Al alloy, with the peak-aged specimens presented the highest corrosion resistance.

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Structural and vibrational properties' study of Arsenic Sulfide chemical species

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In the present research work we investigate the structure and vibrational modes of the Arsenic Sulfide chemical system. Off-resonant Raman spectra were calculated, measured, and analyzed. Structural units, representative of the above system structure (molecular and/or network-like), were optimized at CAM-B3LYP/TZVp theoretical level providing also vibrational spectra in very good agreement with experimental data. Raman spectra were interpreted based on the harmonic frequencies and the activities of vibrational modes obtained by the DFT analysis.

Molecular and network-like structures consist mainly of ($AsS_{3/2}$) pyramids and (S-As-$S_{3/2}$) quasi-tetrahedral units. Their As-S bond lengths and arsenic/sulfur atomic charges have been correlated with chemical environment. The vibrational spectra (Raman and IR) have been recorded and analyzed as they can provide insight about the atomic arrangement over the short- and medium-range structural order. For a more rational and quantitative description of the spectra the use of the reduced Raman spectra is essential.

Changes of the Raman spectra reveal that appreciable structural changes take place upon variation of As/S atomic ratio.

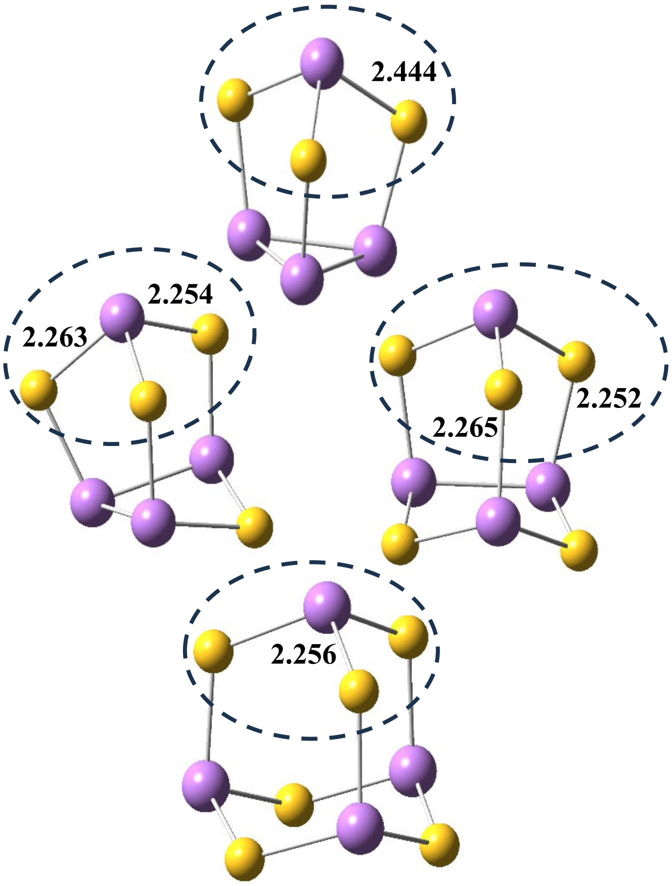

Figure. Ball and stick draws of the CAM-B3LYP/TZVp fully optimized As-S structures.

‘Pincer’ Complexes with N-Heterocyclic Carbene and Related Donors

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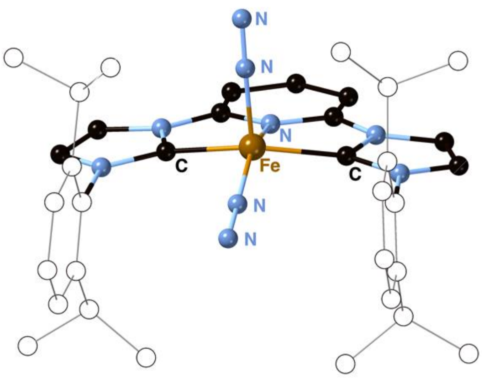
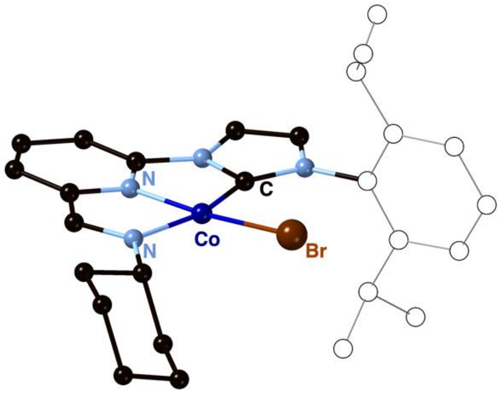
Abstract: The use of ‘pincer’ type tridentate ligands to tune the coordination sphere, the structures (geometric, electronic) and, consequently, the chemical, (photo)physical, physiological and magnetic propeties of the metals is a topical area of interest with potential applications in catalysis (including photo- and electro-catalysis), materials chemistry and medicinal chemistry. In this presentation the focus is on the synthesis and some reactivity of ‘pincer’ complexes with one or two NHC donors(s) at the wingtip(s) and one pyridine donor at the bridgehead positions of the ligand.





Emphasis will be on recent contributions with some ‘green’ 3d transition metals, *i.e.* Cr, Fe and Co. Aspects of ligand design, proton responsiveness and redox non-innocence are going to be presented, which may imply unexpected ‘pincer’ complex speciation of relevance to potential applications.

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The Spin Relaxation Properties of Some Mononuclear S=2, Fe(II) Complexes.

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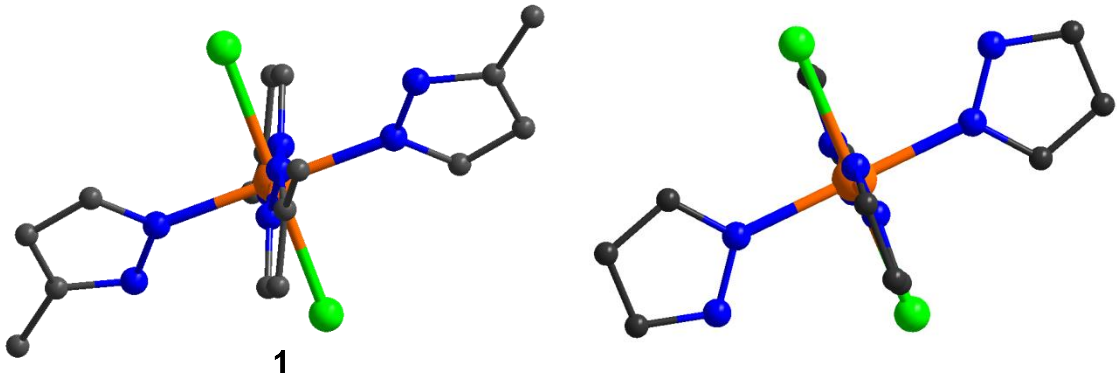
We study the magnetic relaxation properties of three air-stable, mononuclear complexes of the general formula *trans*-[$FeX_2(pz\text{-}R)_4$] (pz = pyrazole and **1**: X = Cl, R = CH_3; **2**: X = Cl, R = H; **3**: X = Br, R = H) (Figure). These complexes contain 6-coordinate Fe centers with N_4X_2-coordination spheres. The zero field Mössbauer spectra from powder samples of **1** – **3** at 80 K comprise fairly narrow doublets. The isomer shift values, δ, for all complexes are consistent with an S=2, Fe(II) ion in an octahedral environment. The quadrupole splitting value, ΔE_Q, for **1** is *ca.* 2.2 mm/s at 80 K and exhibits significant temperature dependence. This behavior is typical for an S=2, Fe(II) ion in an octahedral environment. For **2** and **3**, however, ΔE_Q ~0.5 – 0.6 mm/s and it is practically temperature independent. Theoretical calculations indicate that these differences relate to the different orbital ground state for the three complexes. These different orbital configurations affect critically the spin relaxation properties of the three complexes as monitored by dynamic magnetic susceptibility methods at liquid helium temperatures in the presence or absence of an external magnetic field. Complex **1** relaxes fast whereas **2** and **3** exhibit slow relaxation.



1

2, 3

Figure. The structure of the mononuclear complexes **1-3**. Gray: C; blue: N; green, Cl, Br; orange, Fe.

Coordination properties of Cu(II) ions towards peptide fragments located at the microtubule-binding domain of the longest tau isoform

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Tau protein hyperphosphorylation is a pivotal characteristic of Alzheimer's disease, a progressive neurodegenerative disorder. Tau protein is normally involved in stabilizing microtubules, which are essential for maintaining the structure and transport within neurons. However, hyperphosphorylated tau loses its effective microtubule-binding ability. Consequently, it aggregates, forming neurofibrillary tangles (NFTs), a hallmark pathological feature of Alzheimer's disease. Copper is an essential trace element engaged in various biological processes, including neuronal function and development. Nevertheless, an imbalance or dysregulation of copper homeostasis has been implicated in the pathogenesis of Alzheimer's disease. The role of Cu(II) in these processes, particularly its potential impact on regulating tau phosphorylation and dephosphorylation, remains incompletely understood [1-2]. In recent work, we studied the binding properties of Cu(II) with a short phosphorylated peptide that models the R1 domain of the tau protein. A notable discovery from this investigation was that the phosphorylation of serine residues influences the peptide's affinity for metal binding [3]. Continuing our research in this field, our focus turned to the interaction of Cu(II) with longer peptide fragments (R4/R4P) located within the microtubule-binding domain (MBD) of tau. These peptides exhibited efficient binding with Cu(II) ions, utilizing the N3 imidazole atom as the anchor site for the metal, followed by successive deprotonation-coordination of three amide donors. The potential biological consequences of the strong Cu(II) binding and the peptides-Cu(II) binding affinity differentiation (Fig 1) will also be discussed.

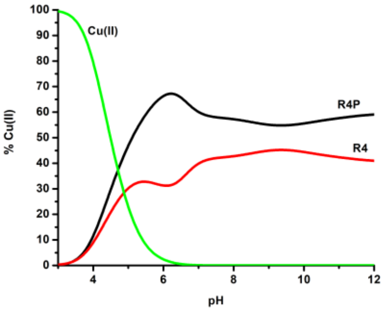

Figure 1. Cu(II) ion distribution in a model system of R4/R4P/Cu(II) in a 1:1:1 molar ratio.

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Low-Dimensional Organic-Inorganic Hybrid

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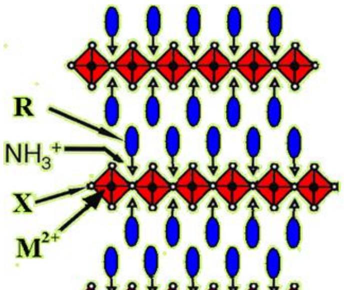
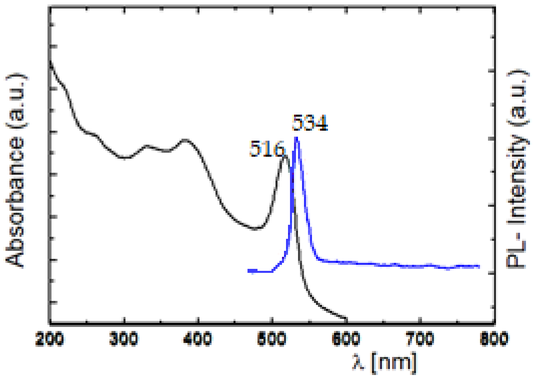
Organic-inorganic hybrid materials have received increasing interest in recent years due to their properties originating from their hybrid character. These materials combine the properties of inorganic semiconductors with the flexibility and low temperature preparation and formulation of organic chemistry.

Especially the hybrid halide perovskites of Pb and Sn have emerged as one of the most promising next-generation photovoltaic materials with high power conversion efficiencies and excellent properties that can potentially drive down the cost of clean and renewable solar energy conversion.

Additionally, to the most known three-dimensional perovskites, similar hybrid materials with low dimensionality can be prepared. By using appropriate molecular design and easy chemical synthesis, two-, one-, and zero-dimensional materials with desired dimensional sizes can be produced. Due to their low-dimensional character and the difference in dielectric constant between the organic and the inorganic-semiconductor parts, strong quantum and dielectric constraints are presented. As a result of these constraints, stable excitons with large binding energies are created that remain bound to the inorganic part, imparting interesting optical and electronic properties.

These low-dimensional hybrid materials present a series of advantages such as flexibility of molecular design, non-linear optical properties, energy transfer from the organic to the inorganic part, tunable energy spectrum, large fluorescence quantum yields, large absorption coefficients in the UV–vis region, increased solubility, ease of preparation of thin films, etc. Another advantage is that they can be easily manufactured with cheap raw materials that are abundant in nature using simple chemical methods.





The use of metals other than Pb and Sn can expand our abilities and give materials with additional properties.

With the appropriate molecular design, we can prepare materials with the desired dimensionality, structure and properties. The design and synthesis of hybrid organic-inorganic materials of various metals, their structure, their properties (with an emphasis on optics) and their technological applications will be the subject of this talk.

η^6-Arene Ru(II) Complexes as Efficient Catalysts for Transfer Hydrogenation of Aromatic Ketones

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Ruthenium(II) complexes comprising η^6-arene ligands, constitute a class of compounds that has been widely used in the transfer hydrogenation reactions of various substrates [1]. The coordination sphere, around the metal center may be filled by a number of different organic compounds such as NHCs, phosphines, quinoline based N^N ligands [2] etc.
In this work, we describe the synthesis and characterization of a series of ruthenium(II) organometallic complexes of the general formula $[Ru(\eta^6\text{-p-cymene})(L)Cl]PF_6$, where L stands for pyridylquinoline- or biquiinoline-based bidentate ligands (Figure 1). It's worth mentioning that there are no previous reports on the coordination/organometallic chemistry of most of the organic ligands reported herein. Characterization includes FT-IR, ^{1}H and ^{13}C NMR, 2D NMR spectroscopy, UV-Vis, elemental analyses, as well as single-crystal X-ray diffraction studies. All complexes significantly catalyze the transfer hydrogenation of acetophenone, and other substrates, in the presence of a base. The complexes reported herein display almost quantitative conversions after approximately 30 minutes. The catalyst's load was 0.025 mmol % and additional 10 mmol % of KOH added in the reaction system. All reactions took place at 83 °C and 2-propanol was used as a solvent and a hydrogen donor.

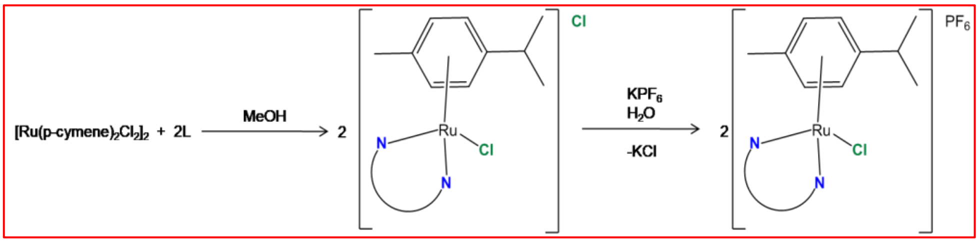

Figure. Synthetic procedure of the Ru(II) complexes described in this work.

[1] D. Wang, D. Astruc, *Chem. Rev.*, **2015**, *115,* 6621.
[2] N. Zacharopoulos, PhD thesis, National and Kapodistrian University of Athens, Grece (2022).

Acknowledgements: A.I.Philippopoulos would like to thank "The Special Account for research Grants of NKUA" for financial support.

Manipulating arene interactions in 1st row transition phenoxide metal complexes.

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Manipulating and enforcing metal-arene interactions by virtue of ligand design has opened new avenues in controlling small molecule activation events[1]; moreover, the propensity of the arene ligand to act as an electron density store[2] can have implications in catalytic transformations involving redox steps.[3] To further understand the intricacies of these advantageous metal-arene interactions, we have developed a new class of ligands with pendant arylo-oxide substituents connected by an arene ring at an apical position poised to interact with a metal centre (Figure 1). These ligands can be prepared in good yields and quantities using a general synthetic protocol, allowing access to different substitution motifs of the pendant aryl-oxide arms to the crucial central arene ring with concurrent variation of other steric and electronic properties.

This new library of ligands has been coordinated to first row transition metals *via* a simple transamination reaction (Figure 1), furnishing a series of new organometallic complexes displaying varying geometries. Structural investigations have shown that the adopted geometries are dependent on the ligands' steric hindrance and ability to enforce different η^x ($x = 1,6$) modes between the central aromatic ring and the metal centre. Combined with preliminary spectroscopic, computational and electrochemical investigations, the ability of these scaffolds to act as redox non-innocent ligands upon traversing the series of 1st row transition metals (Cr, Fe, Co, Ni) has been assessed.

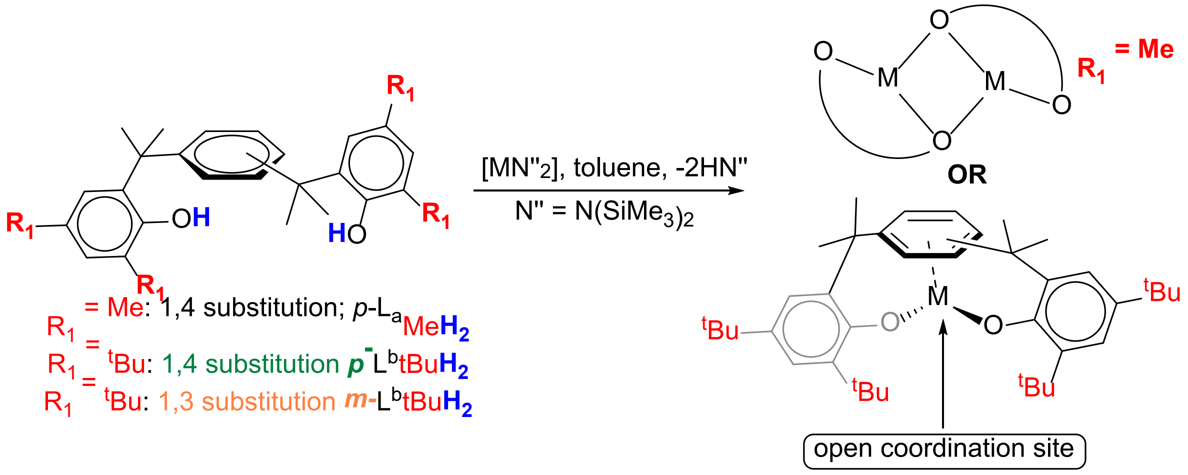

Figure 1. Synthesis of bis-phenoxide arene complexes in unusual geometries.

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POSTERS

Enhancing the Performance of CNT@CoZn-MOF Anodic Electrodes for Hybrid Supercapacitor Cells through CNT Pre-treatment

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Summary

This research focuses on improving the performance of supercapacitors by combining carbon nanotubes (CNTs) with CoZn metal-organic frameworks (MOFs) in a hybrid electrode material. The study explores three different pretreatment methods for CNTs and synthesizes CoZn-MOF using hydrothermal techniques. The combination of CNTs and CoZn-MOF enhances conductivity and specific capacitance, making the supercapacitor more efficient.The most promising results are observed with CNTs treated with acetic acid, which exhibit high specific capacitance and exceptional stability. Even after 3000 charge-discharge cycles, this hybrid supercapacitor retains 88% of its initial capacitance. This study highlights the advantages of incorporating CNTs in supercapacitors and emphasizes the importance of pretreatment techniques. It also offers insights into improving the capacitive performance of MOF materials, contributing to the development of high-performance hybrid supercapacitors for various energy storage applications.

Synthesis and Characterization of Metalloporphyrins and NC-Dots Hybrids for Photocatalytic Hydrogen Production

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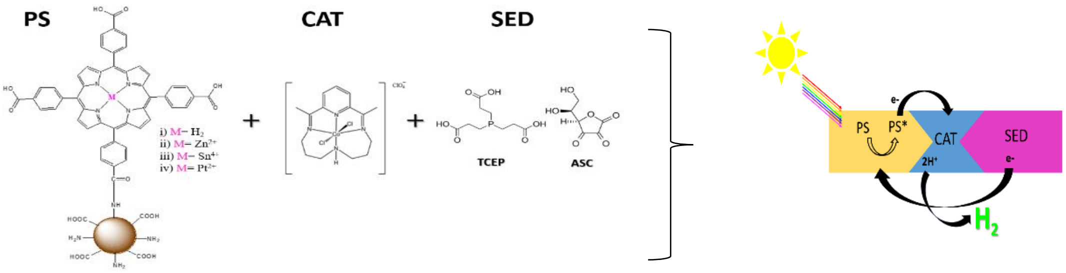
The planet is in the midst of a fast-paced global energy crisis, due to the reckless and extensive use of fossil fuels. An effective and environmentally friendly method proposed by scientists around the world is the photocatalytic hydrogen production system, since during hydrogen production, the only combustion product produced is water. More specifically, such a system consists of a photosensitizer (PS), a catalyst (CAT) and a sacrificial electron donor (SED). The outstanding advantage of porphyrins is that they have an extended aromatic conjugation system which allows them to have intense absorption bands in the visible region. NC-dots have excellent electron transport and optical properties, but their absorption is limited to the visible region. Therefore, in this work, we synthesised and studied the performance of a novel system comprised of metalloporphyrins covalently attached to NC-Dots via an amide bond in order to increase their absorption range. A cobalt molecule was used as a catalyst a cobalt catalyst was used and an aqueous solution of ascorbic acid and a phosphine (TCEP) (1:1) as SED, at pH= 5. A study was carried out to find the optimal photocatalytic system, at different concentrations (20, 50, 100 nmol). The photocatalytic experiments were carried out under visible light irradiation and the expansion of the absorption range of NC-Dots was demonstrated. Overall, the most efficient photocatalytic system studied was the Pt-TCPP-NC-Dots hybrid and 10 nmol catalyst, yielding 734 TONs. This result shows the double role of platinum, as a photosensitizer and catalyst, yielding the best possible performance to the system.



Acknowledgments
The Special Research Account of the University of Crete is gratefully acknowledged for the financial support of this research.

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Exploring the Combined use of Di-2-Pyridyl Ketone with selected diols in Manganese Coordination Chemistry

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Polynuclear coordination complexes of paramagnetic 3d metal ions have become the focus of intense investigation over the last few decades since they often possess interesting physical properties and fascinating structural features. In addition, such compounds can behave as single molecule magnets (SMMs) displaying slow magnetic relaxation of molecular origin due to a significant energy barrier (U_{eff}) to reversal of the magnetization vector.

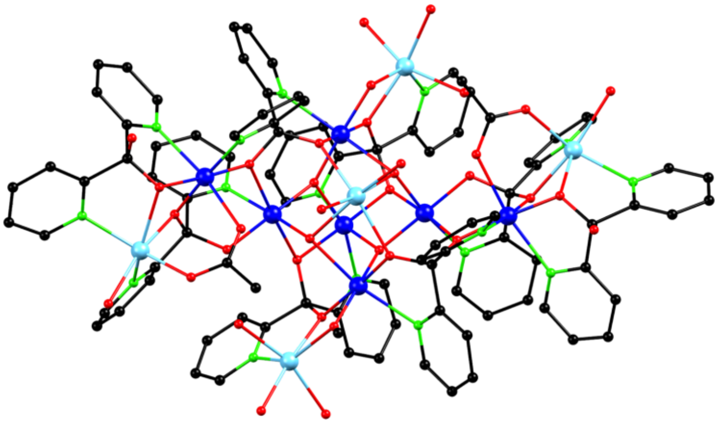

Figure 1: Molecular structure of a representative compound discussed in this work. Color scheme: Mn^{II}, cyan; Mn^{III}, blue; O, red; N, green; C, black. Hydrogen atoms are omitted for clarity.

A crucial parameter in the design of coordination complexes is the choice of the organic ligand because the latter dictates the structure and topology and, therefore, the properties of the resulting compounds. One of the ligands that have been successfully employed in metal cluster chemistry is di-2-pyridyl ketone ($(py)_2CO$), which has a fruitful coordination.[1] Herein, we report the synthesis, structural and magnetic characterization of the results obtained from the combined use of $(py)_2CO$ with selected (poly)alcohol-type ligands (Figure 1). The reported compounds possess rare nuclearities and unprecedented structural motifs as well as interesting magnetic properties.

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Acknowledgements: This work was supported by the Cyprus Research and Innovation Foundation Research Grant “EXCELLENCE/0421/399” which is co-funded by the Republic of Cyprus and the European Regional Development Fund.

Sonochemical synthesis of a novel, stable Ce(IV) Carboxylate-bearing MOF for rapid removal of Pb (2+) from water.

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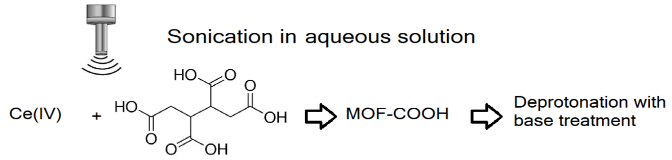
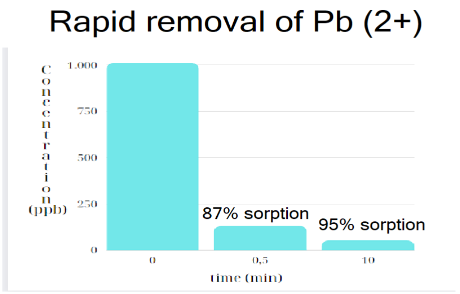
From ancient Rome to the industrial revolution and modern times, lead and other heavy metals have been extensively used in numerous applications. However, as multiple studies over the last century have indicated, chronic or sometimes acute exposure to high concentrations of these pollutants can cause severe damage to the central nervous system, leading to coma, convulsions, and even death.

Metal-organic frameworks (MOFs) represent an emerging class of functional porous hybrid crystalline materials that, for the past two decades, have garnered significant research interest due to their modular structures, unique tunability, and chemical stability. These materials, owing to their sorption capabilities, have been proven to exhibit remarkable efficiency in key applications such as gas storage, gas and liquid separations, and the removal of ionic pollutants, typically heavy metal cations, from water. In the latter category, Metal-Organic Frameworks with free carboxylate groups (MOFs-COOHs) have demonstrated substantial sorption potential, primarily due to the metal complexation capability of carboxyl groups.

Here, we present a novel MOF with free carboxylic acid groups, specifically a Ce(IV)-MOF with 1,2,3,4-butane tetracarboxylic acid, obtained through sonochemical synthesis. This compound has shown outstanding Pb2+ sorption capabilities. Specifically, batch sorption studies have revealed approximately 95% removal of lead cations within 10 minutes and approximately 87% within 30 seconds. Similar results were obtained in in a pH range of 4–8 and Pb2+-polluted natural mineral water samples.





Acknowledgements

This research has been co-financed by the European Union NextGenerationEU under the call RESEARCH – CREATE – INNOVATE 16971 Recovery and Resilience Facility (project code: TAEDK-06193).

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Fine-tuning of the Macrocycle Cavity and Denticity in a Series of Hexagonal Bipyramidal Dy(III) Complexes

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The search for new molecules exhibiting slow relaxation of magnetization under a plausible blocking temperature is currently one of the most appealing research topics in the interdisciplinary fields of inorganic and coordination chemistry, materials science, physics, and theoretical chemistry. Lanthanide(III) ions play a pivotal role in the quest for efficient single-molecule magnets with potential applications in memory storage, molecular spintronics, and quantum computation. This is mainly due to the large magnetic anisotropy that most 4f-metal ions possess, which arises from the strong spin-orbit coupling and the crystal-field effects from the coordinated ligands.[1] Seeking for new synthetic strategies towards the preparation of single-molecule magnets (SMMs) with large energy barriers for the thermally-assisted relaxation of magnetization, the focus of our research is placed around mononuclear Dy^{III} complexes with designed ligands suitable to yield the targeted coordination geometries (D_{5h}, D_{6h}) and subsequently reducing the efficiency of the through-barrier relaxation pathways.[2] Herein, we report the synthesis, structural and magnetic characterization of a new family of mononuclear, air-stable Dy^{III} SMMs, by employing the macrocyclic effect and successfully promoting an N_6, N_3O_3, and N_4O_2 equatorial ligation around a single Dy^{III} ion resulting from a [1+1] metal-assisted condensation reaction (Figure 1). As a result, we have been able to chemically engineer new coordination compounds with hexagonal bipyramidal geometries, bearing strongly bound axial ligands and exhibiting SMM behaviors with large U_{eff} values.

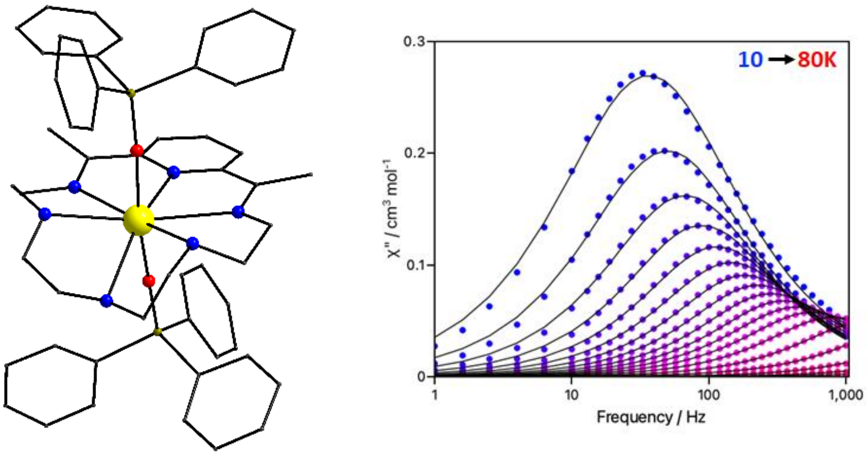

Figure 1: Molecular structure and ac magnetic dynamics of a representative complex discussed in this work with the formula **$[Dy(L^{N6})(Ph_3SiO)_2]PF_6$**. Color scheme: Dy=yellow; O=red; N=blue; C=grey; Si=olive. Hydrogen atoms are omitted for clarity.

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Erbium(III) complexes with third-generation quinolones: Structure and biological activity

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Quinolones are a class of broad-spectrum synthetic antibacterial medications and are clinically used to treat patients with a variety of bacterial infections, in order to repress the bacterial enzymes DNA-gyrase and topoisomerase IV. Third-generation fluoroquinolone medicines such as levofloxacin and sparfloxacin act efficiently against both gram-positive and gram-negative bacteria, by focusing on DNA-gyrase. Because of their high bioavailability, they have been used for the therapy of patients with lower respiratory tract infections such as pneumonia, bronchitis and chronic obstructive pulmonary disease [1]. Quinolones have a noteworthy capacity of binding to common lanthanide(III) ions and forming complexes with improved bactericidal activity, which derives from particular chemical characteristics of these metals [2]. In addition, it has been observed that erbium(III) complexes with Schiff bases and substituted salicylaldehydes have portrayed higher antibacterial and radical scavenging activity [3].

The erbium(III) complexes with levofloxacin (Hlevo) and sparfloxacin (Hsf) were synthesized, characterized and monitored for their biological activity (interaction with calf-thymus DNA, affinity for bovine and human serum albumin, antimicrobial activity against a variety of microorganisms).

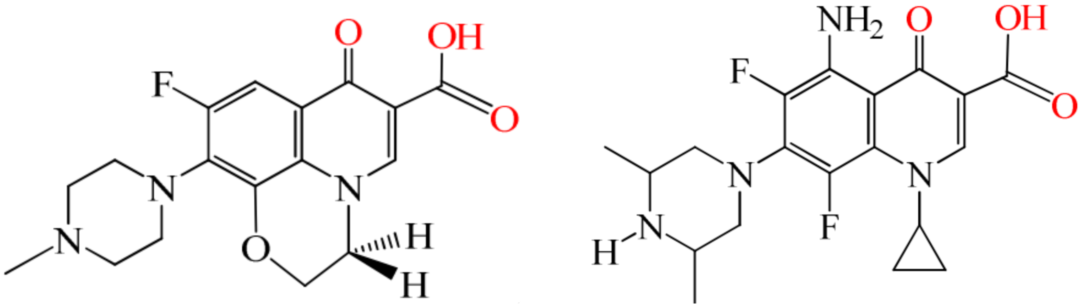

Figure. The quinolones Hlevo (left) and Hsf (right).

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Acknowledgements: This research was conducted as a part of the MSc thesis of author E.A. according to the curriculum of International Graduate Program in “Biological Inorganic Chemistry” that operates at the University of Ioannina with the collaboration of the Departments of Chemistry of the University of Ioannina and the Aristotle University of Thessaloniki.

Molecular Heterometallic Dy^{III}-Bi^{III} Clusters: An Approach to Structurally Unique Compounds with Single-Molecule Magnetic Properties

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The heterometallic chemistry of 3d/4f-metal ions has flourished over the past few decades, providing new structural motifs of nanosized molecular clusters, multifunctional compounds combining two or more physical properties within the same entity, and high-spin molecules with record spin values, as well as single-molecule magnets with enhanced magnetic dynamics. The analogous chemistry of 4f-metal ions with a post-transition metal ion, such as the pnictogen Bi^{3+}, has not been systematically explored, although Bi^{3+} possesses high principal quantum number valence orbitals (6s), and strong spin-orbit coupling. These features create different effects on crystal field and magnetic exchange interactions with metal centers, when compared with the properties arising from the 3d-metal ions, and hence, Bi^{3+} could -in principle- contribute to the enhancement of the molecular magnetic anisotropy [1]. Nevertheless, from a synthetic perspective, it is definitely not straightforward to incorporate both lanthanide(III) and bismuth(III) ions within the same molecular compound since both of these metal ions are oxophilic, they exhibit similar ionic radii and adopt large coordination numbers with a variety of coordination geometries. Given these challenges, and the lack of any previously reported Dy^{III}-Bi^{III} heterometallic clusters to date, we decided to explore the Dy^{III}-Bi^{III} chemistry in order to obtain molecular compounds with interesting structural and physicochemical properties. Herein, we report on the self-assembly synthesis and characterization of a new $\{Dy^{III}_3Bi^{III}_8\}$ cluster bearing the Schiff base ligand *N*-salicylidene-o-aminophenol [2], and its deliberate organization into an 1-D analogous chain via replacement of terminal halides with end-to-end azido groups (**Figure 1**).

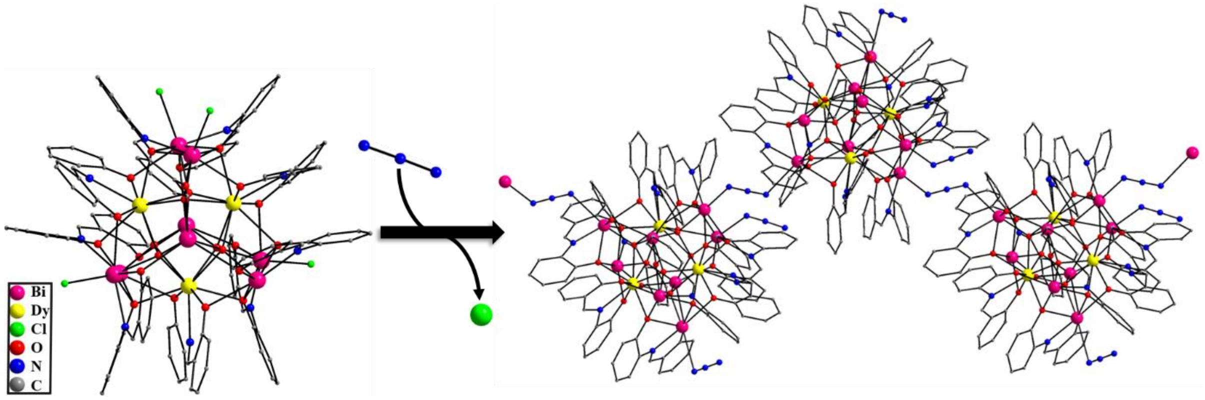

Figure 1. The $\{Dy^{III}_3Bi^{III}_8\}$ cluster (left) and its analogous 1-D chain (right).

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Mononuclear, low-coordinate lanthanide(III) complexes exhibiting single-molecule magnet behavior

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A highly effective approach to elevate the magnetization reversal barrier (U_{eff}) of mononuclear lanthanide single-molecule magnets (SMMs) with an oblate/prolate electron density of the 4f orbitals is to establish a robustly axial/equatorial coordination environment, respectively [1]. The axial character of the ligand field exerts control over both the magnitude of U_{eff} and the likelihood of quantum tunneling of magnetization (QTM) between the energetically favorable magnetic states. The ability to enforce axial symmetry stands as a crucial factor in governing the sluggish magnetic relaxation and, consequently, facilitating the attainment of elevated blocking temperatures [2]. Indeed, the strategic design of rare earth complexes guided by these principles has yielded remarkable strides in blocking temperatures (T_B), particularly in the case of mononuclear Dy(III) SMMs with structures approaching the $C_{\infty v}$ and $D_{\infty h}$ point group symmetries. Herein we report the synthesis and magnetic characterization of three new octahedral (O_h) lanthanide(III) complexes with general formula $[\mathrm{LnI_2(TPPO)_4}](\mathrm{I_3})$ (Ln = Dy **(1)**, Er **(2)**, Yb **(3)**, TPPO = triphenylphosphine oxide), bearing weakly-coupled $\mathrm{I^-}$ groups in the axial positions (**Figure 1**). Hence, the oblate Dy analogue did not reveal any SMM behavior while the prolate Yb complex exhibited slow relaxation of magnetization in the presence of a small external dc field (800 Oe) and one of the highest energy barriers ($U_{\mathrm{eff}} \approx 45.5\mathrm{K}$) recorded for Yb-based SMMs.

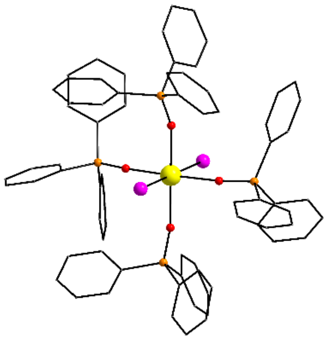

Figure 1. General structure of the cationic complexes **1**-**3**.

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Acknowledgements:
This research was supported by the Andreas Mentzelopoulos Foundation in the form of a scholarship to G.P.B.

Nitrogen-Carbon dots@TiO_2 nanocomposites: Synthesis, characterization and photocatalytic/antibacterical properties under visible light irradiation

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Titanium dioxide (TiO_2) has been widely studied as a nano-photocatalyst material with numerous advantages, including its stable physical and chemical properties, non-toxicity, and simple preparation method [1]. However, its main drawback for direct exploitation of solar-light-based effects is its large band gap of >3 eV. To address this limitation, visible-light-activated TiO_2 can be improved through the incorporation or decoration with other nanomaterials, and semiconductors [2]. One promising category in this direction is carbon quantum dots decorated by nitrogen groups. Nitrogen-Carbon QDs (N-CQDs) differ from traditional semiconductor quantum dots or other carbon-based nanostructured materials (e.g., activated carbon, graphene, and carbon nanotubes) in that they combine the unique optical/photonic properties of quantum dots with the excellent electrical properties of sp^2 carbon-based materials [3]. Furthermore, N-CQDs exhibit low cytotoxicity, are inexpensive and easy to prepare, and possess a high emission quantum yield (QY) [4].

In this study, we synthesized and characterized nanocomposite materials of N-CQDs@TiO_2 with varying amounts of N-CQDs doped into TiO_2. All nanocomposites were characterized using various spectroscopic techniques, such as FT-IR, UV-Vis, PL, XRD, TGA, and SEM. In order to study the photocatalytic activity of these nanocomposites, they were used as catalysts for the photodegradation of Methylene Blue (MB) under eco-friendly LED lamps as visible light source. Finally, they were tested for their antibacterical activity against selected bacteria under visible light irradiation.

Acknowledgements

This research is co-funded by the Special Research Account of NKUA and by Greece and the European Union (European Social Fund-ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning 2014-2020» in the context of the project "Innovative Titanium Nanoparticles for Development of autocleaning and Auto antibacterial Application" (**MIS 5131364**).

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Ti(III) and Ti(IV) as a probe of establishing bonding in NHC carbenes

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Nikolaos Tsoureas

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In the present research work, Ti(III) paramagnetic and Ti(IV) diamagnetic complexes bearing1,3-bis(3,5-di-tert-butyl-2-phenoxy)-5,5-dimethyl-3,4,5,6-tetrahydropyrimidin-ylidene dianionic pincer ligand (L), the latter originating from the corresponding pyrimidinium chloride precursor, (LH_3Cl) by triple deprotonation (Fig.1) have been targeted with the aim of probing the metal-NHC donor bonding and the reactivity of the paramagnetic metal center with various substrates.[1,2] The octahedral [trans-$Ti^{III}Cl\{\kappa O,\kappa C,\kappa O\text{-}L\}(thf)_2$] (**1**) (Fig.2A) and the tetrahedral [$Ti\{N(SiMe_3)_2\}\{\kappa O,\kappa C,\kappa O\text{-}L\}$] (**2**) (Fig.2B) have been fully characterised and served as starting materials for other (TiL) complexes including phenoxides, siloxides and alkyls. The complexes amongst other methods were characterised by EPR- and NMR-spectroscopies, UV-Vis-spectroscopy and crystallographic diffraction methods. A key feature of the Ti(III) complexes is their paramagnetism ($S = ½$). Analysis of their cw EPR spectra or **1** and **2**have afforded the corresponding *g* values, whereas pulse EPR methods are to be employed in order to investigate metal-ligand super-hyperfine interactions,[3] and hence probe the delocalization of unpaired electron density onto the ligand framework.

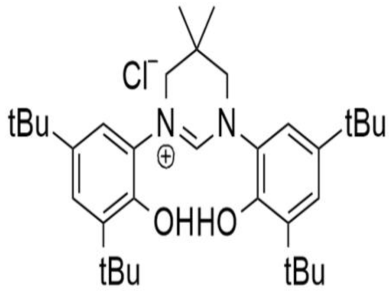
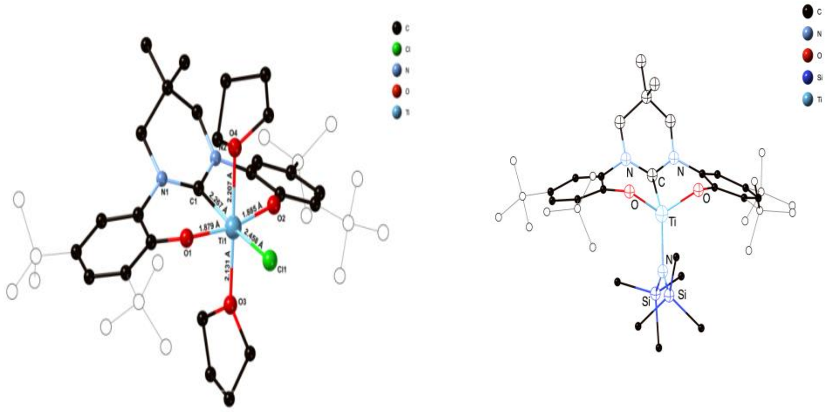


Figure 1: LH3Cl



Figures 2A and 2B: Crystallic structures of (**1**) and (**2**) respectively

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Polyurea-crosslinked iron alginate aerogels and magnetic carbon aerogels

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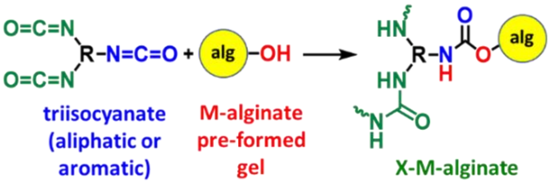
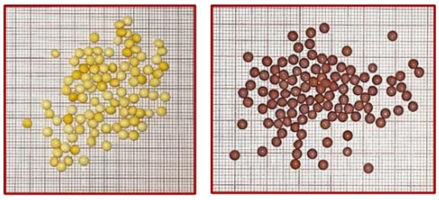
Polyurea-crosslinked iron alginate (X-Fe-alg) aerogels were prepared from the reaction of preformed Fe-alginate gels with aliphatic and aromatic triisocyanates, by applying the X-aerogel technology, initially developed for silica and other inorganic aerogels, in order to prepare polyurea-crosslinked alginate (X-alginate) aerogels [1-3]. They are macroporous (mostly) and mesoporous materials, with low bulk densities (0.033-0.088 g cm^{-3}), high porosity (94-98% v/v) and high BET surface areas (100-313 m^2 g^{-1}).

Magnetic carbon (X-Fe-C) aerogels were prepared from pyrolysis of the aromatic X-Fe-alg aerogels under inert atmosphere (Ar), at five temperatures, i.e., 400, 600, 800, 1000 and 1200 ^{o}C. They are microporous materials (83-87% of the total surface area is assigned to micropores) and they can adsorb CO_2. The optimum materials, in terms of properties and CO_2 sorption, are the aerogels prepared from pyrolysis at 1000 ^{o}C; their specific and micropore surface areas are equal to 314 m^2 g^{-1} and 274 m^2 g^{-1}, respectively, and the CO_2 sorption was equal to 3.3 mmol g^{-1}. All X-Fe-C aerogels are magnetic, indicating the presence of metallic iron and/or magnetic iron oxides (magnetite, maghemite).





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Synthesis, characterization and properties evaluation of encapsulated phase change materials in silica nanospheres as an energy storage systems

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Nanomaterials are materials of the order of nanometers in size, and feature additional or different unique properties compared to their corresponding macroscale materials. This study focuses on phase change materials (PCMs) exploiting their special properties, with the aim of using them as an alternative means of energy storage. In particular, these are systems that store latent heat (LHTES). For this purpose, PCMs are mainly used, which show a phase change from solid to liquid, as they have a high energy density (100 – 400 J/g).

However, this class of materials has got a number of disadvantages, consequently, problems arise regarding their practical application. The elimination of these drawbacks, but also the enhancement of their characteristics, is achieved with the help of containers, which are going to host the PCMs. The process by which this is achieved is called encapsulation. The new composite PCMs, are now called "shape stabilized PCMs". Depending on the application that the PCMs will participate in, their containers may vary in size and shape. This allows them to be utilized by a plethora of applications in all areas of human society.

The present study aims to create porous silica nanospheres in order to act as containers for PCM. Three kinds of phase change materials were encapsulated. In particular, D-mannitol, erythritol and dimethyl terephthalate were selected, which are all organic PCMs. Encapsulation was done by mixing solutions from each PCM and from the spheres, with subsequent stirring and final removal of the solvent.

The identification of the various characteristics of the nanospheres, which will host the aforementioned materials, was done using various methods. Among them, in order to ascertain the morphological characteristics of the spheres, the SEM method was used. Also, in order to have more comprehensive conclusions regarding the size of the spheres and the range they cover, a DLS analysis was performed. In order to calculate the percentage of encapsulation in PCMs, the analytical techniques FT-IR, UV-vis and the thermogravimetric analysis (TGA) were used. Furthermore, thermal cycles were carried out with the DSC method to calculate the thermal stability of the selected materials and also to identify their possible leakage. Finally, an experiment was carried out with the MTT method to determine the metabolic activity of the cells when they come into contact with the materials under study, to determine their toxicity in healthy cells (HEK-293, human embryonic kidney cells.

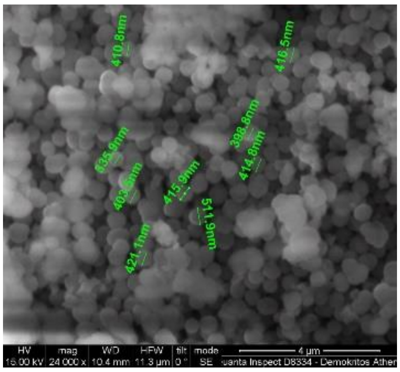

Figure 1: SEM image of porous silica nanospheres.

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Synthesis, structural, magnetic and spectroscopic characterization of chiral heterometallic Cu/Ln complexes with Schiff base ligands

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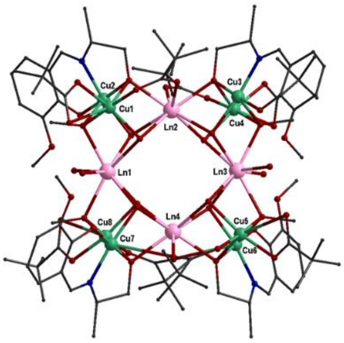
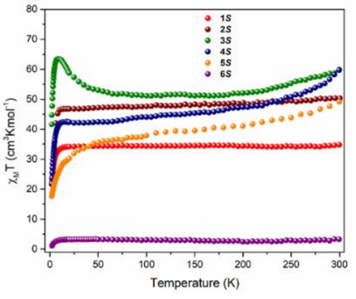
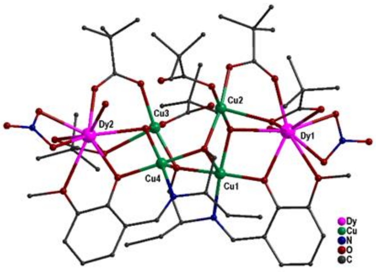
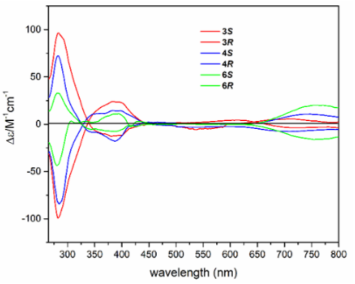
Chirality is one of the core research topics in materials science, chemistry, physics, biology and medicine, and more recently nanoscience for emerging technologies and applications [1,2]. Materials which combine chirality with physical properties, such as magnetic, optical, catalytic behavior, within the same moiety, which also maintain their properties at the smallest possible level, are useful for applications. Molecular chemistry is the best-suited route towards the synthesis of such multifunctional materials. Metal clusters are prepared by a bottom-up approach based on coordination chemistry principles. More specifically, heterometallic 3d/4f coordination clusters combine the electronic properties of the respective 3d metal ions with the anisotropy induced by the lanthanides, and by the use of proper chiral ligands constitute a class of magnetochiral materials for potential applications. The use of chiral ligands ensures chirality to the derived complexes which is imparted to the crystal structures which crystallize in non-centrosymmetric polar space groups.

We will discuss the synthesis, structural, magnetic and optical characterization of families of heterometallic Cu/Ln (Ln^{III} = Gd, Tb, Dy, Ho, Er and Y) complexes based on chiral Schiff base ligands.









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New Eu^{III} Complexes as Luminescent Solar Concentrators

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In recent years there has been a noticeable shift in scientists' efforts to use solar energy for encountering the rapid increase in global energy consumption and the simultaneous need to reduce the environmental impact of fossil fuel-based energy sources. Photovoltaics (PVs) is one of the most remarkable and active applications designed to take advantage of the enormous amount of energy provided by the sun and convert it directly into electricity. The application and use of luminescent solar concentrators (LSCs) is expected to lead to future reduction of the overall cost and other advantages over traditional PV cells, such as, reduction of the weight and bulk of the device, ability to coordinate the color and operate efficiently even under diffuse light [1]. Organic dyes, quantum dots (QDs), transition metal and lanthanide (Ln) ions can be used as optical active centres in LSCs. Ln^{III} -and particularly Eu^{III}- complexes with organic chromophore ligands are excellent candidates for application in LSCs devices, not only because of their large Stokes shift (>200 nm) compared to organic dyes and QDs, but also because of their comparatively high quantum emission efficiency. One of the major challenges in this filed is the selection of the appropriate ligands and the prevention of quantum yield degradation by incorporating the coordination complex into an organic-inorganic hybrid matrix or polymer, which ensures the photostability of the active optical centers and their easy processing into thin films [2].

Herein, we have synthesized, and structurally, spectroscopically and optically characterized new Eu(III) complexes bearing the chelating ligands 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ) and thenoyltrifluoroacetonate (TTA$^-$) (**Figure 1**). These ligands were proved effective for energy transfer in the excited states of several lanthanides. The optical studies led to the conclusion that these complexes are quite promising luminescent active entities which can be applied as optical active centers in LSCs devices.

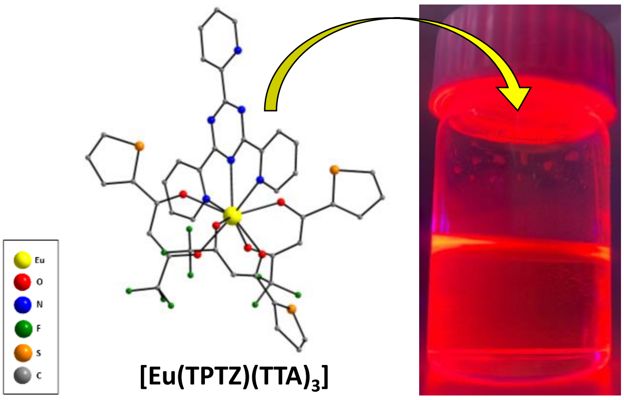

Figure 1. The molecular structure of [Eu(TPTZ)(TTA)$_3$] and its red luminescence in solution.

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A Safe-by-Design approach for the production of low toxic, widely applied inorganic nano-oxides.

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Nanotechnology has revolutionized peoples' living standards by introducing unique consumer products. Nanosilica (SiO_2) materials are among the most applied nanostructures, produced industrially in tons per year and found in pharmaceuticals, cosmeceuticals, food, energy, automotive, electronics, telecommunications, fiber optics, and computer technology. Despite their unique advantages, this widespread use also raised concerns about potential impacts on ecosystems and human health[1.] This research introduces novel synthetic roots to produce safer-to-use nano-SiO_2 materials utilizing the Flame Spray Pyrolysis (FSP) technique and post-FSP mild chemical treatments. Concurrently, a detailed analysis of the structure-toxicity relationship (SAR) of pure and hybrid nanosilica materials (see Fig. 1) has been carried out implementing Raman and Electron Paramagnetic Resonance (EPR) spectroscopy, in tandem with biocide activity studies towards marine bacteria *Aliivibrio Fischeri.* Technology-wise, the present work exemplifies controllable processes for the industrial production of applied nano-oxides[2] while contributing to the long-anticipated issue of SiO_2 toxicity.

Figure 1. ROS-induced and structure-related toxicity of pure and hybrid nanoSiO_2 materials.

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Acknowledgments: We acknowledge the support of this work by the project "Center For Research, Quality Analysis Of Cultural Heritage Materials and Communication Of Science" (MIS 5047233), which is implemented under the Action "Reinforcement of the Research and Innovation Infrastructure," funded by the Operational Program "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).

Photophysical properties of supramolecular organometallic platinum(II) complexes with p-biphenyl and derivatives of 4,4´-bipyridine

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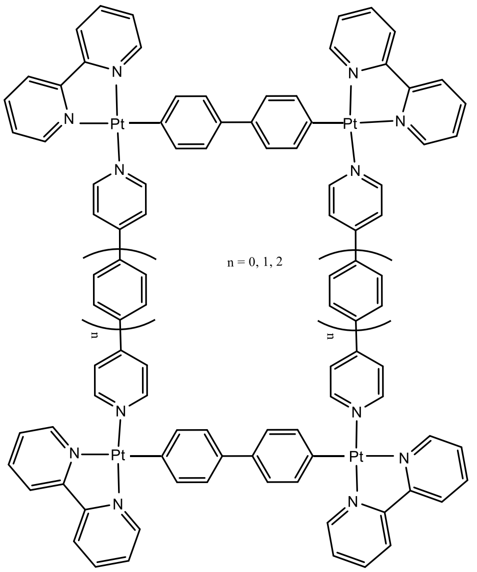
The remarkable attributes of supramolecular tetranuclear platinum(II) complexes have attracted significant research attention. Their structural characteristics make them highly promising for various applications, such as anticancer agents,[1] DNA binders[2], drug delivery vehicles[3] and luminescent agents. These complexes are frequently employed as bioimagers, driven by metal-to-ligand charge transfer processes. In recent years, noteworthy advances have been made, with many complexes exhibiting substantial quantum yields[4] or extended excited-state lifetimes[5]. Furthermore, the interaction with various solvents has been found to influence the excitation and emission profiles of these structures[6]. Additionally, the tendency of these compounds to form aggregates has a direct impact on their photophysical properties[6].



Herein, we report on the synthesis and characterization of three novel supramolecular organometallic Pt(II) complexes with 2,2´-bipyridine as auxiliary ligand and 4,4´-dipyridine derivatives, as well as p-biphenyl as bridging ligands with increasing size: $\{[Pt^{II}(2,2'\text{-}bpy)]_4(\mu\text{-}bphen)_2(\mu\text{-}(4,4'\text{-}bpy)_2\}\{PF_6\}_4$, $\{[Pt^{II}(2,2'\text{-}bpy)]_4(\mu\text{-}bphen)_2(\mu\text{-}(4,4'\text{-}bpy(\mu\text{-}bz)_2\}\{PF_6\}_4$, $\{[Pt^{II}(2,2'\text{-}bpy)]_4(\mu\text{-}bphen)_2(\mu\text{-}(4,4'\text{-}bpy(\mu\text{-}bphen)_2\}\{PF_6\}_4$. Also, their luminescent properties, versus the solvent polarity and the aggregation degree, were studied.

Acknowledgements

Antonia Garypidou and Konstantinos Ypsilantis were financially supported by the project “Center for Research, Quality Analysis Of Cultural Heritage Materials and Communication Of Science” (MIS 5047233) implemented under the Action “Reinforcement of the Research and Innovation Infrastructure”, funded by the Operational Program “Competitiveness, Entrepreneurship and Innovation” (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).

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A new Zr (IV) MOF with methyl-thio functional groups for the removal of heavy metal ions from aqueous media

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Nowadays, environmental pollution has risen to be one of the most catastrophic phenomena of the human fingerprint in nature. Toxic polluting ions do have a significant role in carcinogenesis, DNA damage and mutation and their constantly increasing concentration in aqueous media is a threat for every living organism. Thus, there is an immediate need to develop methods for their efficient removal from water resources. Metal organic frameworks are considered some of the most promising tools to accomplish this goal. [1,2] Their porosity, alongside with their facile synthesis, tunable structural features etc., convert them into proficient materials to withdraw toxic ions from water.

Here, we present the synthesis and characterization of a Zr (IV) MOF with a polytopic ligand bearing methyl-thio functional groups. Through detailed batch sorption studies, we demonstrate that this material is a very efficient sorbent for heavy metal ions. Furthermore, we investigated the capability of the MOF to act as luminescent sensor for toxic ionic species.

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NextGenerationEU

Acknowledgements

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Synthesis, structural and photophysical characterization of heteroleptic Ag(I) complexes with aromatic diimines and triphenylphosphine

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Luminescent mononuclear Ag(I) complexes are a class of compounds that have attracted considerable interest due to their potential use as sensors, photocatalysts, emitters in light-emitting devices, etc. The most studied of these incorporate various chelating diimine-type ligands (NˆN) and phosphines (P or PˆP) [1].

Ag(I) complexes often show long-lived phosphorescence originating from ligand-centered excited states (^{3}LC) and rarely exhibit TADF (Thermally Activated Delayed Fluorescence). The nature of the excited state in heteroleptic Ag(NˆN)(PˆP) type complexes (LL'CT, and/or MLCT) strongly depends on the electron donating properties of both ligands, while the insertion of bulky substituents at positions located near the coordinating atoms (N and/or P) generally increases the photoluminescence quantum yield (Φ_{PL}) [2].

In this report, we will present the preparation, structural characterization and the photophysical properties of three novel heteroleptic Ag(I) complexes containing the phosphine PPh_3 and 2,9-disubstituted 1,10-phenanthroline derivatives (Fig. 1)

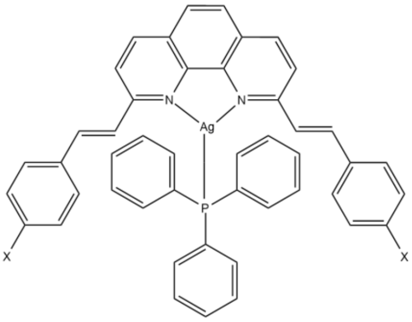

Figure 1. Schematic representation of the structure of the studied Ag(I) heteroleptic complexes (X=-OMe, -SMe, -NEt_2)

[1] H. Takeda, A. Kobayashi, K. Tsuge, *Coord. Chem. Rev.*, **2022**, *470*, 214700.
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Acknowledgements: The authors would like to thank The Network of Research Supporting Laboratories at the University of Ioannina for providing access to use MS, NMR and X-ray diffraction facilities.

A Zr(IV)-metal organic framework-cotton composite with thiophene functional group for the removal of gold nanoparticles from aqueous media

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Noble metal nanoparticles (NPs) are among the most widely used colloidal systems in nanoscience and nanotechnology. Their unique properties have led to a rapid increase of their production and use in a variety of products and applications in industry, medicine and pharmacology, treatment of water and pollution control, etc. However, as the manufacturing and use of noble metal NPs is rising, their environmental levels and the eco-toxicological risks are expected to increase, due to their occurrence in waste waters and natural waters. Hence, noble metal NPs have been classified as emerging contaminants due to their potential environmental and health impacts. As a result, there is an increasing interest in their removal from water. In this study we report the use of Metal Organic Frameworks (MOFs) supported on cotton textiles (MOF@cotton) as a sorbent phase of gold nanoparticles (AuNPs) from water. Specifically, a water stable, 8-connected Zr(IV)-MOF with a new dicarboxylic ligand bearing a thiophene functional group, named MOR-3 (Figure), was irreversibly immobilized on polydopamine decorated cotton fabric. In this manner, it was possible to achieve the combination of the permeability of the host cotton substrate with the high specific surface area and sorption capacity of the MOF. The sorption efficiency of the MOF@cotton composite was examined in various water media (lake, river, seawater) with satisfactory results. Furthermore, it shows good sorption capacity (~ 152 mg Au / g MOF x m^2 cotton, as 4 nm AuNPs) and good sorption efficiency for AuNPs of variable size and surface functionalization (i.e. AuNPs coated with polymers, biomolecules, small organic molecules, etc) indicating its wider applicability as a sorbent phase of AuNPs from water samples. The potential recovery of AuNPs after sorption was also examined with satisfactory results (79 to 109%).

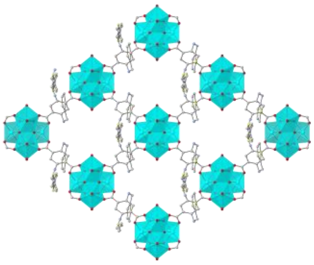

Figure. Representation of MOR-3 down to b axis. (Zr : cyan, C : grey, N : blue, O : red.)

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Synthetically controllable magnetic anisotropy of transition-metal Prussian Blue Analogs with composition $Co_3[Cr(CN)_6]_2 \cdot xH_2O$

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Prussian Blues (PBs) and their analogs (PBAs) are an especially amazing and evergreen family of compounds. Recent investigations of the chemistry and physical properties of PBs have stimulated an astonishing rebirth of interest in the magnetism of complex solids and a revival of the chemistry of inorganic cyanide chemistry. PBs and PBAs can be synthesized by the reaction of hexacyanometalates $[B(CN)_6]^{p-}$ with transition metal Lewis acids A^{q+} in water to give neutral three-dimensional networks of the type $A_p[B(CN)_6]_q \cdot nH_2O$. PBAs are discussed for a large range of applications, such as negative-thermal expansion materials, sensors, gas separation devices and hydrogen-storage applications, to name just a few. Also, some of the PBAs generated some interest for potential magnetic applications due to the possibility of photomagnetism. Magnetic order is possible because the bridging cyanide ligands may allow for indirect exchange (superexchange) between the magnetic ions, which may be in either low- or high-spin configurations due to crystal field effects. We will present, for the first time, a citric acid-assisted protocol for synthesizing the PBA with composition $Co_3[Cr(CN)_6]_2 \cdot xH_2O$, where various experimental conditions were explored, influencing critically the size and morphology of the final PBA nanoparticles (NP). This investigation revealed a well-controllable synthetic mechanism for producing PBA $Co_3[Cr(CN)_6]_2 \cdot xH_2O$ particles with sizes ranging from 1500 – 100 nm. The phase purity of the products was determined by X-ray diffraction, revealing a cubic $Fm\bar{3}m$ structure. Magnetic measurements showed a long-range magnetically ordered state at critical temperatures close to 23 K while an apparent increase of the magnetic coercivity is observed from values H_c=300 Oe for microparticles to H_c=600 Oe for PBA NPs with sizes close to 100 nm corroborating the influence of the size to the magnetic anisotropy of the PBA.

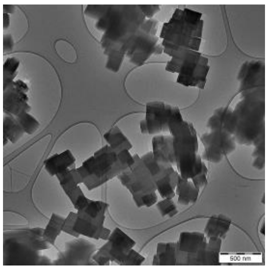

Fig. 1. Experimental TEM image of $Co_3[Cr(CN)_6]_2 \cdot xH_2O$ particles with a size of 100 nm.

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The effect of metal hydroxides on silica scale formation: Relevance to geothermal systems

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One of the biggest problems in the geothermal industry is the deposition of inorganic precipitates (crystalline or amorphous) on critical equipment that is in contact with geochemical fluids. Common precipitates include metal sulfides, amorphous silica and metal silicates, the latter including silicates of aluminum, iron and magnesium. Colloidal/amorphous silica ($SiO_2 \cdot xH_2O$) is one of the most undesirable deposits in the water treatment industry. It is not as widespread as other mineral scale deposits (eg. $CaCO_3$), but its formation and deposition onto critical equipment surfaces can be catastrophic.

Its inhibition and control is mainly based on two approaches: (a) removal of "soluble" and colloidal silica before entering the system, and (b) use of scale inhibiting chemical additives. Silica formation is further complicated by the presence of metal hydroxides (commonly iron, aluminum, and magnesium hydroxides). The scope of the present study is to explore the effects of the presence of such hydroxides on silica formation. Several experimental variables were evaluated, such as nature of the metal ion, particle size, solution pH and temperature.

Metal (Mg or Al) silicate formation can follow two mechanisms: (a) Mg^{2+} and Al^{3+} species can directly interact with silicate and catalyze its polycondensation to amorphous silica. (b) Soluble silicate can deposit on $Mg(OH)_2$ or $Al(OH)_3$ surfaces. The second pathway appears to be much slower than the first. Nevertheless, although the second mechanism (silicate deposition onto metal hydroxide solid particles) is less likely to take place in industrial waters, it was worth-investigating. Both $Mg(OH)_2$ or $Al(OH)_3$ surfaces (from externally-supplied solid metal hydroxides) can accelerate silicate polymerization, but at slower rates, with $Mg(OH)_2$ being much slower than $Al(OH)_3$. Particle size dramatically affects the formation of silica, as expected. Smaller particles create larger surfaces for interaction with soluble silicate, and thus, induce faster silicate polymerization.

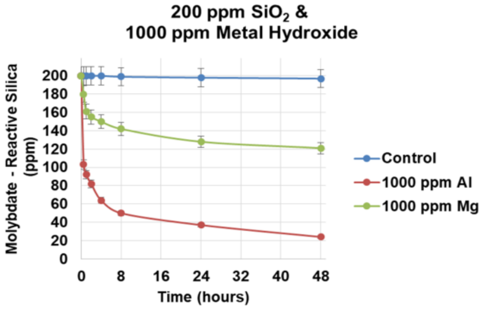

Figure. Molybdate reactive silica (ppm) from solution at 200 ppm initial silicate concentrations, at 1000 ppm initial $Al(OH)_3$ and $Mg(OH)_2$ concentrations.

Novel photocatalytic materials for dye degradation using adsorbed porphyrins on 3D printed structures

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The growing issues associated with environmental pollution and energy shortages posing serious threats to humans and nature. A promising technique for the decomposition of contaminants in water is photocatalysis. In photocatalytic procedure light promotes appropriate energy to the catalyst where then it excites electrons (e^-) from the valence band to the conduction band, generating photo-induced electron and hole pairs. These photo-generated electron and hole pairs contribute to advanced oxidation reactions for the partial or full degradation of contaminants. Numerous porphyrins have already been used efficiently as photosensitizers in various applications such as H_2 production, CO_2 reduction and in dye degradation applications.[1] Nevertheless, it is difficult to control their structure precisely, since they self-assemble in homogeneous media. Therefore, immobilization of porphyrins on solid supports can enhance their properties. Three-dimensional (3D) printing is a new technology that has been used in numerous fields of science and could find application in water purification. More specifically, it is possible to design structures with a large external surface able to deposit a photosensitizer and maximize the photocatalytic effect.[2] In this research, various tetraphenyl porphyrins (H_2TPP, ZnTPP, *o*-H_2TPP(NH_2)$_4$, PPyPP) are deposited on 3D printed structures and their reactivity in water with various dyes (Methylene Blue, Reactive Black 5) is tested with visible light irradiation. The results are quite promising since under certain conditions *o*-H_2TPP(NH_2)$_4$ degrades Methylene Blue dye in just 100 minutes.

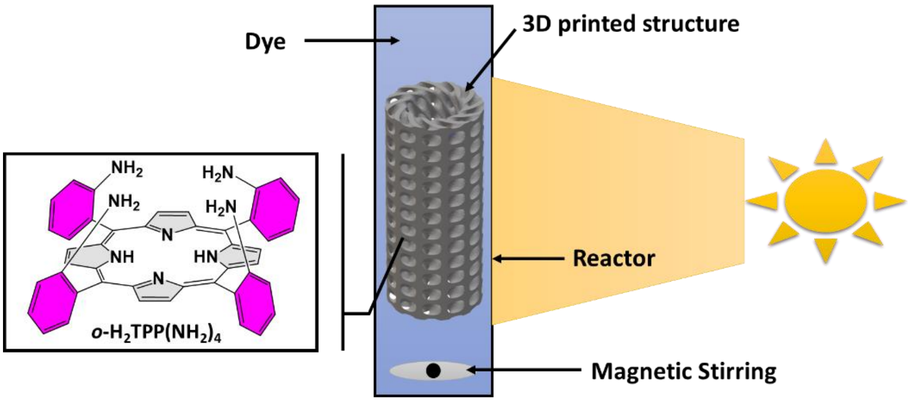

Figure 1: 3D printed reactor with adsorbed porphyrins.

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Multiphoton Laser Ablation using methacrylic polymer thin films doped with Silver nanoparticles

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In this work, directly exposing poly(methyl methacrylate) (PMMA) thin films doped with, oleylamine protected Silver nanoparticles is demonstrated, using a continuous wave 405nm diode laser source. Thin solid films prepared by spin coating were structurally characterized using UV-VIS, FT-IR spectroscopy as well as SEM microscopy. The presence of surface plasmon resonance peak, characteristic of silver nanoparticles at 450 nm in UV-VIS absorption spectra of Ag-PMMA films confirms the formation of Ag-PMMA nanocomposite. TEM characterization showed Ag nanoparticles of average size 10 nm embedded in PMMA matrix. SEM images of the Ag/PMMA film revealed very good dispersion of Ag nanoparticles into the PMMA matrix. If the radiation flux exceeds a certain threshold, the Ag nanoparticles transfer the absorbed light energy into the PMMA matrix leading to the polymer degradation and ablation resulting the creation of hole-like patterns in the sub 200 nm regime.

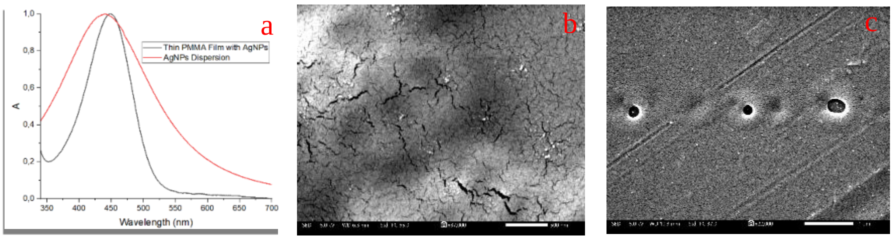

Figure. a) UV-VIS spectra of the toluene dispersion of Ag NPs and the thin film of Ag/PMMA and SEM images of b)the surface of Ag/PMMA and c) Laser Ablation of Ag/PMMA

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SYNTHESIS AND APPLICATION OF HETEROATOM-CO-DOPED CARBON DOTS IN PHOTODYNAMIC THERAPY OF SQUAMOUS CELL CARCINOMA

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Carbon dots (CDs) are a new type of carbon-based nanomaterials with increasing research interest in various applications such as solar cells, photocatalysis, nanomedicine, sensing, etc. CDs demonstrate properties such as non-toxicity, superb water solubility, and strong photostability that make them attractive candidates in bio-related applications, including photodynamic therapy (PDT) [1],[2]. Heteroatom doping constitutes a flexible and facile approach to tune and improve CD's properties and structure with the introduction of new surface functional groups [3]. This work presents the synthesis of heteroatom-co-doped CDs and their potential use in PDT against squamous cell carcinoma. We report the hydrothermal synthesis of nitrogen-boron (N,B-CDs), nitrogen-phosphorus (N,P-CDs), and nitrogen-sulfur (N,S-CDs) co-doped CDs and investigate their photophysical properties with UV-Vis and PL spectroscopy, as well as their ability to generate reactive oxygen species (ROS). FT-IR spectroscopy was also employed to examine the additional functional groups on CDs surface from the heteroatom doping. The optical properties and structure of CDs differ depending on the heteroatom, and all of the synthesized nanomaterials were capable of producing ROS. The CDs did not exhibit dark toxicity in cells and showed enhanced PDT effect based on in vitro cell studies using the human epidermoid carcinoma A431 cell line, highlighting CDs as a promising photosensitizing drug.

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Post Synthetic Modification of UiO-66-NH_2 MOF, using acyl chlorides via solution and mechanical routes.

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Metal Organic Frameworks (MOFs) are coordination polymers consisting of metal ions or metal clusters acting as nodes and organic ligands acting as linkers. Due to the nature of the metal nodes and the organic functional groups (-OH, -NH_2, etc.), they can be used in numerous applications. One application in which MOFs can be used is wastewater remediation. In this case strong bonds between the metal ion and the organic ligand are required while the latter should contain a suitable functional group.

In this work we focus on heavy metal cation (Pb^{2+},Hg^{2+},Cd^{2+}, etc.) sorption from an aqueous environment. Our approach creating a suitable MOF for this application depends on the post synthetic modification (PSM) of an already known MOF which bears an amine group and can be further react with an acyl chloride forming an imide bond. This procedure can take place either in an anhydrous solution (i.e. THF) or in a mechanochemical jar. The final MOF contains -COOH groups and we believe that this modification will enhance the sorption of the parent MOF (UiO-66-NH_2) towards heavy metal cations.

Acknowledgements: Single crystal and powder diffraction data were collected in the National and Kapodistrian University of Athens X-ray Diffraction Core Facility.
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L-Lysine passivated Carbon quantum dots for the enhancement of the TiO_2 nanoparticles' photocatalytic and antibacterial activity under visible light

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TiO_2 nanoparticles are the most common photocatalysts nowadays, due to their high catalytic activity, their photostability, non-toxicity and also because of their one pot and low cost synthesis. The high recombination rate of electron-hole pairs and their low absorption in visible light are factors that block this photocatalytic activity.[1,2]There are many ways to enhance the photocatalytic performance of TiO_2 nanoparticles, one of them is the creation of nanocomposites with semiconducting materials that can absorb into the visible region and also can suppress the recombination electrons and holes.

On the other hand carbon quantum dots, CDs, are small semiconducting and biocompatible nanomaterials known for their high photoluminescence, photostability. CDs are consist from a carbon core and a variety of functional groups on their surface that could interact with many other nanomaterials and create different types of new hybrid materials. Depending on the reaction conditions, their size and visual properties could be adjusted.[3] The passivation of CDs with amino acids, AAs, such as L-Lysine imparts higher QYs to the conventional fluorescent dyes and also a better stability in aqueous dispersions in a broad range of pH.[4]

Herein we report the synthesis and characterization of carbon quantum dots passivated by AAs and the creation of nanocomposites with TiO_2, L-CDs@TiO_2, in many different ratios of precursors. The nanocomposites L-CDs@TiO_2 tested for their photocatalytic activity for degradation of Methylene Blue (MB) under visible light source (LED lamps-20W) and studied for their and antimicrobial activity on St. Aureus and E. Coli colonies in the presence and absence of light. Finally it had been conducted MTT experiments in order to be demonstrated the viability of HACAT cells after the nanocomposites treatment.

Acknowledgements

This research is co-funded by the Special Research Account of NKUA and by Greece and the European Union (European Social Fund-ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning 2014-2020» in the context of the project "Innovative Titanium Nanoparticles for Development of autocleaning and Auto antibacterial Application" (MIS 5131364).

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Bioinspired Catalysts For Light Driven Hydrogen Evolution

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An upcoming challenge to today's society is the elimination of the energy crisis. Many alternatives to the common fossil fuels, are recommended as green energy resources.[1] Hydrogen and its photocatalytic evolution through water splitting, introduces the term of artificial photosynthesis (AP) into the energy production industry.[2] Reducing water to H_2 using a biomimicking catalyst, under visible light conditions, is leading to a more sustainable and also cyclic fuel economy. Inspired by natural catalysts, such as [NiFe] hydrogenases, many complexes containing Ni-S have been designed to imitate this biological catalytic activity.[3,4] Additionally [NiFeSe] hydrogenases containing selenocysteine in place of cysteine at the nickel active centre, display unique properties in water splitting and pave the way to new Ni-Se catalysts.[5] Nickel is seen as a cheap and easily accessible metal that belongs to the platinum group and creates efficient catalysts to be used for hydrogen generation.[6] On the other hand the non-innocent nature of those kind of ligands attached to a nickel-metal center represent this kind of biomimetic catalysts with excessive activity into hydrogen evolution reaction.[7] Herein we present the synthesis and characterisation of nickel catalysts paired with dithiolenes, diselenolenes and thiosemicarbazones and their use in the light driven hydrogen evolution reaction, under visible light LED lamps($\lambda \geq 400$ nm).

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TiO_2 photocatalysts as a new solution for the disinfection of Municipal Wastewater Treatment Plant

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Among key issues in Municipal Wastewater Treatment Plants (MWTP) is the existence of pathogenic bacteria in the discarded effluents [1]. Conventional disinfectants (ozone, UV irradiation, chlorine) have been insufficient in providing safe water, due to the development of undesirable and noxious by-products. TiO_2 comprises an attractive alternative to conventional methods because of its versatility and recently explored biocidal efficiency [2-4]. As a result, within the framework of this study, chemically modified, visible active nanocrystalline TiO_2 powders were prepared *via* a low-cost, feasible sol-gel method for the treatment of real municipal wastewater effluents. Wastewater samples were acquired from the outlet of the treatment of Antiparos (Cyclades, Greece) MWTP during summer period in which a great number of seasonal habitants and tourists usually visits the island resulting to at least doubling of population. All synthesized powders were thoroughly characterized using various morphological and spectroscopic techniques, such as FE-SEM, XRD, micro-Raman, FTIR and DLS. Photocatalytic evaluation experiments were initially conducted towards Rhodamine B degradation under visible light irradiation. The effect of the produced powders on the disinfection as assessed in terms of faucal indicator microorganisms (E. Coli and total Coli forms) inactivation was examined in a semi-pilot scale-up photocatalytic reactor. The results of the present study demonstrate the feasibility for TiO_2 to be utilized as a viable, eco-friendly approach for the photocatalytic pathogenic bacteria inactivation as an alternative disinfection approach for municipal wastewater treatment plant effluents with intense seasonal fluctuations in volume.

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Towards sustainable plastics recycling: assessing the integrity status of polypropylene (PP) debris to recycle marine-degraded materials

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Polypropylene (PP) is a widely used polymer with significant environmental implications when improperly disposed [1], [2]. Effective recycling strategies for PP are crucial for mitigating plastic pollution and achieving sustainability goals [3]. This investigation focuses on classifying PP debris based on their degradation status utilizing absorption spectrometry analysis and tensile testing. The debris are classified based on the above analyses in three distinct degradation groups, based on the induced damage due to environmental exposure. In the present work, the classified PP debris samples are then blended with virgin PP to produce recycled specimens, aiming to enhance their properties and their overall quality. The recycled specimens undergo further evaluation through the same mechanical and chemical analysis. This assessment helps identify the integrity status group(s) with desirable properties and determines the optimal percentage of virgin PP incorporation. The research findings contribute to the development of sustainable and cost-effective recycled PP specimens, promoting circularity in PP plastics.

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A Zr (IV) MOF with thiophene functional group for removal of Pb^{2+} from aqueous media.

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Lead is a highly toxic, non-biodegradable heavy metal, which is involved in industrial processes. As a component of industrial wastewater, it ends up polluting the water resources and affecting living beings by causing serious health problems even death. Metal Organic Frameworks (MOFs), especially Zr^{4+} MOFs, are very promising in Pb (II) decontamination of water thanks to their highly crystalline structures, large pores, structural diversity, variety of functional groups, as well as high thermal and chemical stability[1], [2].

Here we describe an 8-connected Zr(IV)-MOF with a new dicarboxylic ligand bearing a thiophene functional group, named MOR-3, which presents excellent water stability, high crystallinity and relatively large surface area. This MOF could achieve very fast (1 min) and almost quantitative (>99%) Pb (II) removal from aqueous solutions. Furthermore, it shows high sorption capacity (~250mg Pb g^{-1}) and it is excellent sorbent in a wide pH range as well as in the presence of other competitive ions, such as Ca^{2+}, Na^{+} and Mg^{2+}. The Pb(II) sorption capability was efficient in both batch and continuous flow experiments. The regeneration of starting material from Pb-loaded-MOF was achieved through acidic treatment, enabling the reuse of MOF in several cycles.

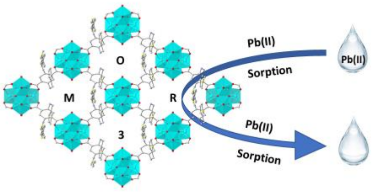

Figure 1: Representation of MOR-3.

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Rationalizing zinc enhancement of natural product neuroprotective potential through molecular chemistry at the biological level

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Neurodegeneration is a debilitating condition (Alzheimer, Parkinson, Huntington) plaguing increasing populations of aging people around the globe. Albeit complex in the etiopathogenesis, organ-specificity in the human body, and often difficult to predict the age of onset and progression, environmental, genetic and lifestyle nutritional habits have over the years emerged as factors affecting the process itself for which there is no cure. Cognizant of the severity of Alzheimer's neurodegeneration and poised to confront the Mild Cognitive Impairment stage of the process, we embarked on the development of molecular metal-organic species of well-known physicochemical profile, interacting with natural product extracts from *Cornus mas L.*, collectively providing protection of neurocellular targets from demise. To that end, zinc-citrate was synthesized and characterized in the solution and solid state, thereby allowing investigation of interactive chemistries with *Cornus* aqueous extracts, when present in sensitive neuronal cell cultures of N2a and SY-SH5Y cells. The well-characterized zinc complex allowed rationalization of its interactions with *Cornus* extracts, thereby exemplifying concentration-dependent (a)toxicity (cell viability, morphology, migration, proliferation), antioxidant enhancement of the natural product influence on neuronal cell survival under oxidative stress conditions, and anti-inflammatory properties exemplified through genetic marker investigation (cytokines, caspases), thereby earmarking the biological molecular chemistry of neuroprotection.

The collective physicochemical profile of Zn-citrate interwoven into the biochemically defined *Cornus mas L.* aqueous extracts, help us understand how it enhances natural product neuronal cell physiology in the human brain, collectively averting and/or retarding neurocellular demise. The advent of such bioinorganic forms of zinc sets the stage for further development of efficient metal-organics to protect, prevent, avert and/or retard human brain neurodegeneration in synergy with natural products.

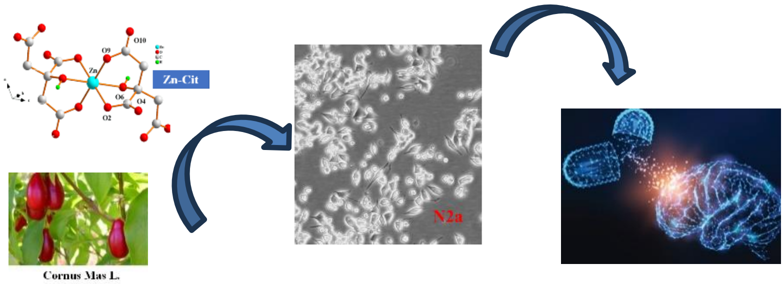

Figure 1. Zn-citrate enhancement of Cornus extract neuroprotection

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Hybrid Silver Iron Oxide Nanoflowers : Synthesis, characterization and their theranostic ability against glioblastoma

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Abstract:

Inorganic nanoparticles have found different applications now days due to their unique properties. By combining the characteristics of different metal nanoparticles hybrid nanoparticles are synthesized combining different desired properties. Among this category are silver – iron oxide nanoparticles, which can combine magnetic properties due to iron and plasmonic properties due to silver[1].

In our work, we synthesize hybrid silver – iron oxide nanoflowers that can be used as a theranostic tool in the treatment of glioblastoma. Hybrid nanoflowers are characterized fully morphologically and structurally, while their synthesis is being tested by varying synthetic parameters to give conclusions on the factors affecting the formation of this unique morphology. Different nanoflowers are obtained when the reaction time and/or Ag/Fe ratio is changed, and the results are compared. Moreover, nanoflowers are evaluated for their cytotoxicity, their hemocompatibility and their ability to internalize into cells monitored by two different protocols[2]. To further modify the nanoflowers by coating, we encapsulate them inside liposomes and red blood cell membranes. Furthermore, to create a multisensitive nanovehicles we co-encapsulate lidocaine as drug of choice and modified their surface with transferrin for enhanced selective targeting against glioblastoma.

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Solvothermal synthesis and crystal structure of two new formate-acetate MOFs based on Ni and Co.

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Metal-Organic Frameworks (MOFs) are porous crystalline materials resulting from the coordination of metal ions or clusters with organic bridging ligands, forming one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) networks with potential voids [1]. While our research primarily focuses on synthesizing MOFs using novel bis-amide ligands, we have successfully synthesized two new MOFs based on acetate and formate anions. It's worth noting that formate and acetate-based MOFs are not novel, as numerous similar MOFs have already been documented [2]. Although 3d transition metals like Fe, Ni, Co, Mn, and Cu are commonly employed, Mg also exhibits potential for creating such MOFs. The utilization of shorter ligands can enhance the metal-oxygen bonding ratio, contributing to a more stable framework. Moreover, we anticipate advanced magnetic ordering due to strong spin-spin interactions between adjacent metal centers.

In this work, we present the solvothermal synthesis and crystallographic characterization, with structural analysis using single crystal and powder X-ray diffraction techniques, of these two MOFs. We are currently awaiting squid measurements to explore the expected magnetic properties of these materials. Additionally, their thermal stability was assessed through thermographic measurements. The two presented MOFs are the 3D $[Ni_{1.5}(HCOO)_{1.75}(AcO)_{1.25}]_n$ and the 2D $[Co_6(HCOO)_6(AcO)_6DMF]_n$.

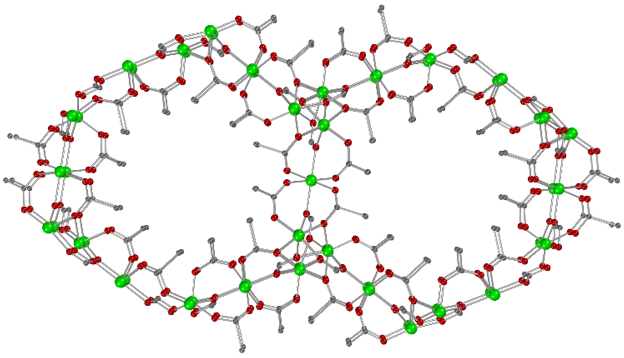

Figure. The channels of the $[Ni_{1.5}(HCOO)_{1.75}(AcO)_{1.25}]_n$ down the crystallographic axis c.

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Acknowledgements: Single crystal and powder diffraction data were collected in the National and Kapodistrian University of Athens X-ray Diffraction Core Facility.

Heterometallic Complexes 3d-4f as Luminescence Thermometers

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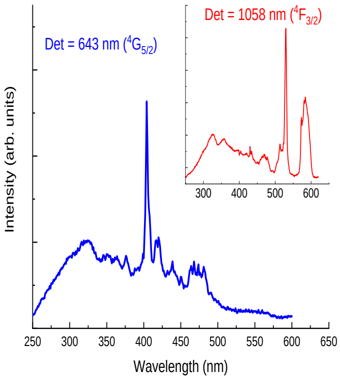
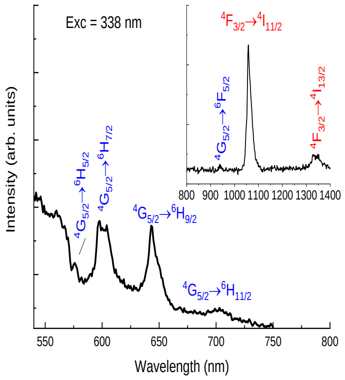
Compounds that show a combination of two or more properties in the same molecule are characterized as multifunctional or "hybrid" molecular materials and are a modern object of research. Complex compounds of some Ln^{III} can combine optical and magnetic properties, so they can be considered as potential hybrid molecular materials. Heterometallic cyano complexes and/or coordination polymers have been shown to combine interesting magnetic properties with other characteristics, such as their microporosity, electrical conductivity, and luminescence. It is well established that derivatives of heterocyclic ligands bearing N-oxide functionalities effectively sensitize the emission. We present the synthesis and study of heterometallic Co^{III}/Ln^{III} cyano coordination polymers that combine optical and magnetic properties. The thermometric parameter defined by optical measurements allows the compound to be used for temperature sensing in the range of 125-300 K.

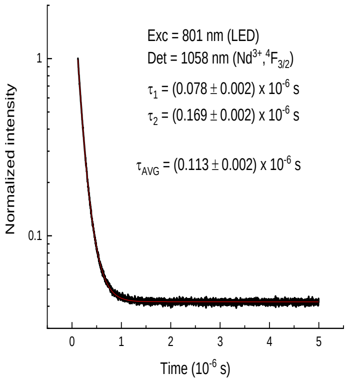
Excitation spectrum



Emission spectrum



Time resolved decay curve



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New synthetic approaches in heterometallic chemistry: Deliberate replacement of trivalent metal ions in a family of $\{M^{III}{}_4Ln^{III}\}$ clusters

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Heterometallic chemistry of 3d- and 4f-metal ions has attracted the interest of several scientists working in the areas of coordination chemistry, molecular magnetism, optics, catalysis, and materials science. The main interest stems from the ability of transition metals and lanthanides, when combined in the same molecular entity, to yield structurally beautiful compounds with exciting magnetic properties, such as single-molecule magnets or molecular magnetic refrigerants. Although numerous 3d/4f-metal cluster compounds have been reported to date, there is still a thirst for the synthesis of high-nuclearity, isoskeletal complexes, where the 3d-metal ion will be deliberately replaced in the polymetallic motif without breaking the core structure but instead altering the physical (magnetic, optical, etc.) properties.[1] It thus seems promising to combine highly anisotropic or isotropic lanthanide ions, e.g. Dy^{III} ($^6H_{15/2}$ ground term) and Gd^{III} ($S=7/2$), respectively, with different trivalent transition metal ions such as Cr^{III} ($S=3/2$) or high-spin Fe^{III} ($S=5/2$), preferably interacted in a ferromagnetic way.[2] In order to study the magnetic contributions of the above spin carriers, we have extended the work by replacing either Cr^{III} and Fe^{III} ions with diamagnetic Ga^{III} centers or the Dy^{III} and Gd^{III} ions with diamagnetic Y^{III} centers. Herein, we report the synthesis, structures and magnetic properties of a family of isoskeletal $\{M_4Ln\}$ clusters, where M = Fe^{III}, Cr^{III}, Ga^{III} and Ln = Gd^{III}, Dy^{III}, Y^{III}, which exhibits a unique 'bat'-like topology (**Figure 1**), resulting from the use of *N*-salicylidene-2-amino-5-chlorobenzoic acid ($sacbH_2$) as a chelating/bridging ligand.

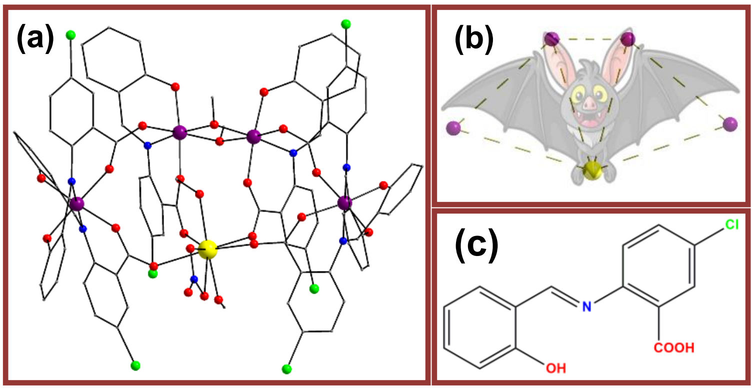

Figure 1. (a) The molecular structure of the isoskeletal $\{M_4Ln\}$ complexes. (b) The 'bat'-like metallic skeleton. (c) The chemical formula of the ligand $sacbH_2$.

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New Family of High-Nuclearity Lanthanide-Titanium-Oxo Clusters as Fine Color-Tuning Luminescent Materials

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In the seek of useful and efficient high luminescent molecular materials, lanthanide-containing clusters have recently attracted great attention, due to their interesting optical properties and their potential applications in the fields of solar energy conversion, material science, LEDs, biological imaging, and luminescence temperature sensors. Compared to homometallic lanthanide complexes, the heterometallic lanthanide-transition metal (3d/4f) clusters, generally exhibit limited fluorescent properties, due to the presence of quenchers, such as coordinated water molecules and hydroxo bridges, that results in the diminish of the luminescence Quantum Yield (QY).[1] Lanthanide-Titanium-Oxo Clusters (LTOCs), combine both the characteristics of Titanium-Oxo Clusters and the unique lanthanide properties, while at the same time exhibit intriguing luminescent properties with long lifetimes and high luminescence QY. [2] To this perspective, we herein report the synthesis, structural, spectroscopic and optical characterization of a new family of high-nuclearity LTOCs with general formula $(Et_3NH)[Ln_9Ti_2O_6(OH)_6(O_2CPh)_{12}(HO_2CPh)_6(hmboxH)_6]$ (**Figure 1**), where Ln^{III} = Eu, Tb, Sm, Dy, and $hmboxH_2$ is the ligand 3-hydroxy-3-methyl-2-butanone oxime.

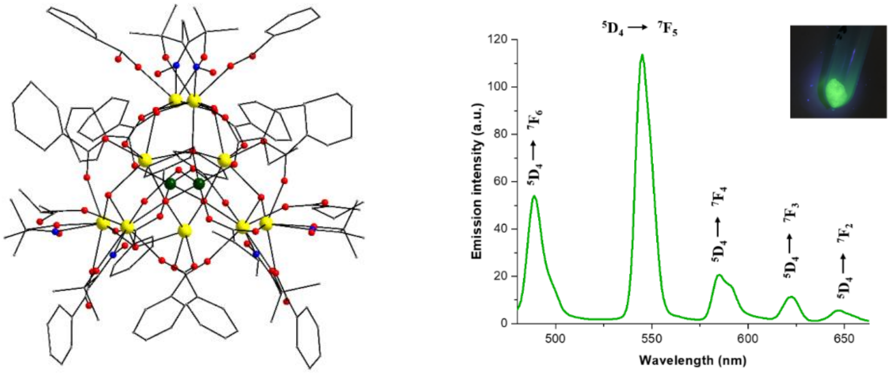

Figure 1: Molecular structure (left) and the PL spectrum (right) of the $\{Tb_9Ti_2\}$ cluster. Color scheme: Tb = yellow; Ti = dark green; O = red; N = blue; C = grey. Hydrogen atoms are omitted for clarity.

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Antibacterial activity evaluation of functionalized TiO_2 nanoparticles with Zn-based Quantum Dots under visible light

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In recent years, bacterial infections in public places like hospitals, have become a great concern for human health. Titania is a widely used standard photocatalyst for environmental applications. TiO_2 nanoparticles are well known for organic dyes degradation, like methylene blue [1]. However, its photocatalytic efficiency is limited in the UV spectra region. The former can be overcome by modifying the electronic band structure of the TiO_2 nanoparticles with Zn-based quantum dots. Herein, their band gap extension to the visible region is currently outlined [2]. Visible light driven functionalized TiO_2 nanoparticles can be used as decontaminant and antimicrobial agents [3].

This work demonstrates the photocatalytic and antibacterial activity of the functionalized TiO_2 nanoparticles, in the visible spectra region. In fact, modified TiO_2 nanoparticles were prepared via a sol-gel synthesis. Morphological, structural, and optical characterizations were investigated using a combination of spectroscopy and microscopy techniques. Moreover, an *in vitro* biological and antibacterial evaluation of the nanoparticles was performed. Photocatalytic degradation of organic dyes was evaluated under visible light. Furthermore, the antibacterial activity of the nanoparticles was assessed.

Photocatalytic, antibacterial and biological assessment of the TiO_2 functionalized nanoparticles indicated enhanced photoactivity and antibacterial behavior of TiO_2 due to modification with Zn-based quantum dots.

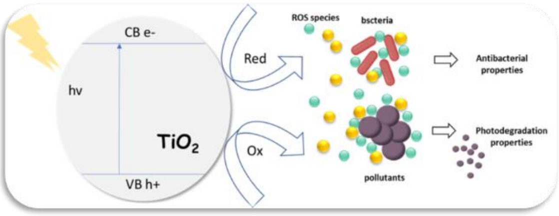

Figure 1: Photocatalytic and antibacterial properties of TiO_2 nanoparticles.

Acknowledgements: This research is co-funded by the Special Research Account of NKUA and by Greece and the European Union (European Social Fund-ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning 2014-2020» in the context of the project "Innovative Titanium Nanoparticles for Development of autocleaning and Auto antibacterial Application" (MIS 5131364).

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The "Periodic Table" of 1-methylbenzotriazole: Efforts to Prepare Tin Complexes

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Benzotriazoles are central "players" in Organic, Medicinal, Environmental and Materials Chemistry. They are also important in Inorganic Chemistry and have been used for the synthesis of coordination clusters and coordination polymers, often with interesting magnetic, optical and catalytic properties [1]. 1-methylbenzotriazole (Mebta) is the archetype of simple N-substituted benzotriazoles with groups that contain no donor sites. Over the past 3 decades, we have been making an effort to create a "periodic table" of Mebta, studying its reactions with as many as possible metal and metalloid ions. We tried to fill the blank space of Sn in this table. The reaction of $Sn^{II}Cl_2$ and Mebta in $CHCl_3$/MeCN under aerobic conditions at refluxing temperature led to the isolation of the ionic, perovskite-type complex $(MebtaH)_2[Sn^{IV}Cl_6]\cdot 2H_2O$ which does not contain Sn^{IV}-N bonds. The structure of the complex was determined by single-crystal X-ray crystallography (Figure, left). The product was characterized by a variety of spectroscopic techniques, including solid-state ^{119}Sn NMR spectroscopy (Figure, right).

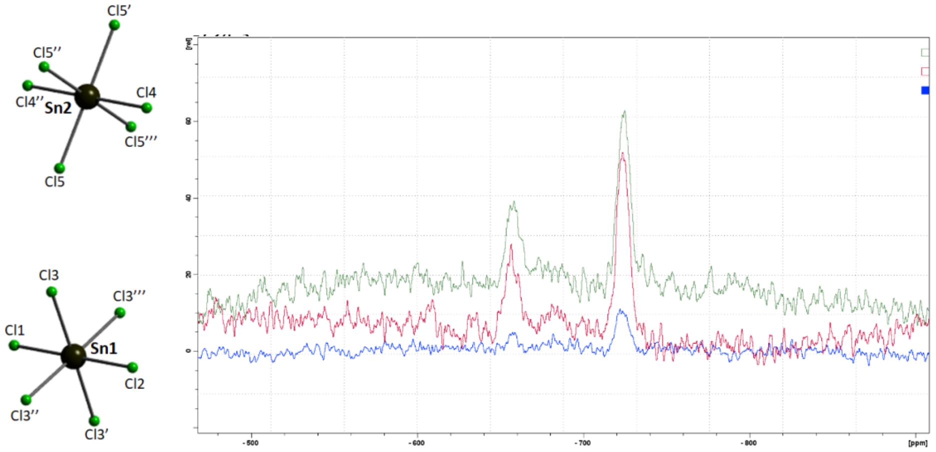

Figure. The two crystallographically independent $[Sn^{IV}Cl_6]^{2-}$ ions, and the solid-state ^{119}Sn NMR spectrum of $(MebtaH)_2[Sn^{IV}Cl_6]^{2-}\cdot 2H_2O$. The latter shows two signals at δ -657.1 and -724.3 ppm, attributable to the two slightly different Sn^{IV} environments.

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Structural features and magnetic properties of M(II), M = Ni, Co, Mn, complexes bearing $\{R_2P(E)NP(E)R_2\}^-$ (E = O, S, Se) ligands

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The structural features and magnetic properties of M(II), M = Ni, Co, Mn, complexes bearing $\{Ph_2P(E)NP(E)Ph_2\}^-$ ligands, E = O, S, Se, are explored. Octahedral complexes were synthesized starting from tetrahedral $[M\{(OPPh_2)(EPPh_2)N\}_2]$, E = S, Se, complexes and also from binuclear $[M_2\{OPPh_2)_2N_4]$ [1] complexes. N-donor ligands such as pyridine, (dimethylamino)pyridine, 4′,4′,bipydisulfide and pyrazine are employed. The factors controlling the Zero-Field Splitting axial (*D*) and rhombic (*E*) components in this family of Ni(II) complexes are explored. The *S* = 1 octahedral *trans*-$[Ni\{Ph_2P(O)NP(E)Ph_2\}_2(sol)_2]$, sol = dmf [2], thf [2], dmso [3], complexes have been shown to exhibit $D > 0$, which precludes them of showing Single Ion Magnet properties, but the sign of *D* is favourably inversed ($D < 0$) in the case of the recently studied $[Ni\{Ph_2P(O)NP(S)Ph_2\}_2(pyrazine)_2]$ complex. In addition, the X-ray crystal structure of the tetragonal pyramidal Ni(II) complex $[Ni\{Ph_2P(Se)NP(Se)Ph_2\}_2(py)]$ prepared from $[Ni\{Ph_2P(Se)NP(Se)Ph_2\}_2]$ [4] will be presented. This is the first complex exhibiting a $NiSe_4(py)$ first coordination reported up to date with this kind of ligands.

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Pincer Complexes of Main Group Metals with N^{amino}-$N^{pyridine}$-C^{NHC} Donors: Synthesis, Characterization, and Catalytic Applications

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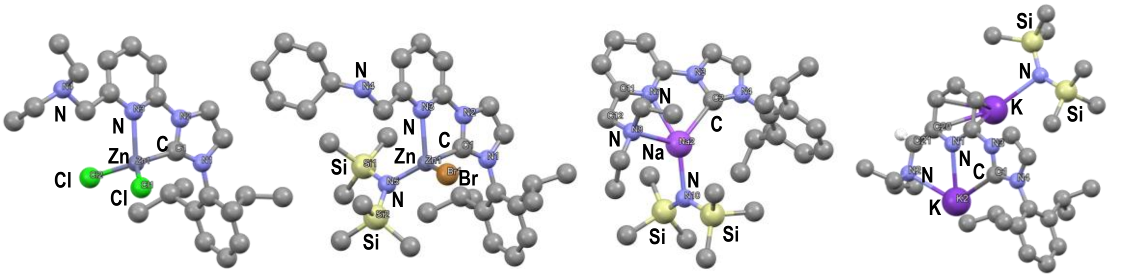
Pincer-type ligands in combination with numerous metals have been continuously generating attention for applications in diverse areas and particularly in homogeneous catalysis, owing to their ability to fine tune the electronic and steric properties of the metal center; the incorporation of *N*-heterocyclic carbenes (NHC) presents additional tuning options, due to the enhanced stability and catalytic efficiency that the NHC donors are known to provide.[1] Meanwhile, efforts have intensified to replace in established catalytic transformations the noble metals with more abundant elements, such as main group metals. Specifically, zinc and magnesium complexes have been used in this respect, in applications such as lactide polymerization;[2] recently, metal-ligand cooperation with dearomatized pincer ligands has been utilized to broaden the scope of their activity in the hydrogenation of imines, ketones, alkenes and *N*-heteroarenes, overcoming redox limitations of the aforementioned metals.[3,4]
With this background, we have synthesized a series of original complexes of main group metals, including zinc, bearing NNC-type ligands.[5] These complexes were characterized by a multitude of techniques including X-ray diffraction crystallography (Figure 1) and NMR spectroscopies; their catalytic activity in lactide polymerization reactions is currently under study. Synthetic efforts and spectroscopic studies involving other main group metals are also discussed.



[ZnCl$_2$(L1)] [ZnBr(N(SiMe$_3$)$_2$)(L2)] [Na(N(SiMe$_3$)$_2$)(L1)] [K$_2$(L1^{dearom})(N(SiMe$_3$)$_2$)]$_n$

Figure 1: Molecular structures of synthesized and characterized main group complexes.

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Synthesis and characterization of MOF-COOHs for water remediation: Pre- and post-synthetic modification approach of amide ligands

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Since the dawn of industrialization, water, the most vital material on earth, has suffered from constant contamination of organic and inorganic compounds. In this study, we focus on heavy metal ion pollution of water supplies, and the ways this can be remediated using Metal-Organic Frameworks (MOFs), a class of hybrid materials consisting of metal ions and organic bridging ligands, giving rise to one, two and even three-dimensional networks. Due to their exceptional stability towards water and other factors, they have been studied as sorbents for heavy metal ions in water purification applications. MOF-COOHs[1] is a term introduced lately to describe MOFs bearing free carboxylic groups decorating the interior of their pore, rendering them more promising for sorption and sensing capabilities.

Our group focuses on three known MOFs from the literature, namely Al-MIL-53(NH_2)[2], Zr-UiO-66(NH_2)[3], Al-CAU-10(NH_2)[4] based on 2-amino-terephthalic acid, for the first two and 5-amino-isophthalic acid for the latter. Our attempts focus on either the post-synthetic acylation of the free -NH_2 group of the ligand with a variety of dichlorides of dicarboxylic acids, or the pre-synthetic acylation of the ligand with the corresponding monochloride or monoesterified derivatives of the same dicarboxylic acids and then undergo hydrolization.

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Acknowledgements: Single crystal and powder diffraction data were collected in the National and Kapodistrian University of Athens X-ray Diffraction Core Facility. This research has been financed by the European Union - NextGenerationEU in the context of the National Recovery and Resilience Plan (Greece 2.0) under the call 16971: RESEARCH – CREATE – INNOVATE (project code: TAEDK-06193).

Magnetoliposomes encapsulated DNR against cervical cancer: Characterization and Biological evaluation

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Nowadays, nanomedicine constitutes a cutting-edge technology for diagnosis and treatment of a wide variety of diseases and especially in cancer. One of the most interesting applications of nanotechnology is the use of liposomes in the field of cancer treatment. Liposomes are spherical vesicles consisting of one or more concentric phospholipid bilayers enclosing an aqueous core. Being both non-toxic and biodegradable, liposomes represent a powerful delivery system for various drugs. The accurate design of liposomal drug delivery systems is undoubtedly an extremely challenging procedure, since it is necessary to take into consideration several factors, such as the type of lipids that are being used, the synthetic methodology, the amount of each lipid, the overall charge and size of liposomes, the type of drug and many others. Except of liposomes, hybrid nanostructures, including liposomes and iron oxide nanoparticles, known as magnetoliposomes, are gaining ground due to their potential as diagnostic and treating tools in different cancer types at the same type. The main application of magnetoliposomes is their use in magnetic hyperthermia treating of cancer, due to their interesting magnetic properties.

In this project, we successfully designed and synthesized two different kinds of magnetoliposomes based on their surface charge (anionic/cationic), encapsulated with anticancer drug Daunorubicin (DNR). Nanostructures mentioned above, were successfully characterized with analytical techniques including DLS, FT-IR, UV-vis and in terms of biological evaluation we investigated their properties according to the MTT assay, Prussian Blue staining and Fluorescence imaging. Finally, we investigated the efficiency of the synthesized structures in comparison with Daunorubicin, a gold standard anticancer drug.

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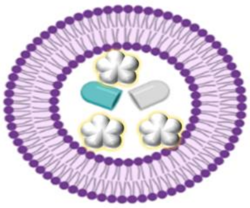

Figure 1: Illustration of hybrid liposomes encapsulated with iron oxide nanoflowers and an anticancer drug

Development of Magnetoliposomes (MLPs) as novel drug nanocarriers for atherosclerosis

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Atherosclerosis is classified as a chronic inflammatory disease and is one of the most common, leading causes of death in developed countries. The objective of the present work was to synthesize and characterize multifunctional iron oxide magnetic nanoparticles, exploiting the nano-size and the colloidal behavior that they have, for the early diagnosis and treatment of diseases related to inflammation, such as atherosclerosis. [1]

More specifically, we successfully synthesized iron oxide magnetic nanoparticles *via* the co-precipitation method, and we encapsulated them in liposomes (Magnetoliposomes MLPs), as well as with the two different, hydrophobic statin drugs, atorvastatin, and simvastatin. With this combination of theranostic MLPs and drugs, we provide a smart theranostic system. MLPs are characterized, in terms of their hydrodynamic diameter, as well as zeta potential. To investigate the cellular uptake of mNPs we used the Prussian Blue assay and also identified the MLPs localization and endocytosis mechanism in Human Umbilical Vein Endothelial Cells (HUVECs). A hemocompatibility assay to improve the non-hemolytic effect of MLPs with RBCs was performed. The magnetic accumulation of MLPs under flow conditions was investigated and their up-take by HUVECs was monitored using a live holotomography system.

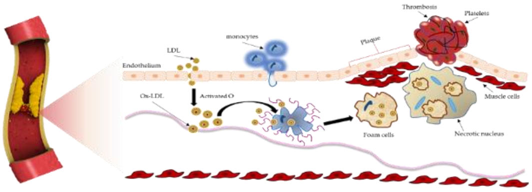

Figure 1. Progression of Atherosclerosis.

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2) Part of this research work was supported by the Hellenic Foundation for Research and Innovation (HFRI) and the General Secretariat for Research and Technology (GSRT), under the HFRI PhD Fellowship grant (GA. no. 14650) and co-financed by Greece and the European Union (European Social Fund- ESF) through the Operational Program « ERANETs 2021A, Action: ERANET RUS PLUS » in the context of the project "Rational design of novel magnetic nanocarriers for targeted vascular therapies" (MIS 5161147).

Computational Study of Structural and Vibrational Properties of the As_4X_y (X= O, S, Se and y= 3-10) molecules

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We report an investigation of the structure and vibrational modes of As_4X_y (X= O, S, Se and y= 1-10), molecular species using first principles calculations. Vibrational spectroscopy, and in particular Raman scattering, is a very powerful experimental tool, which is frequently employed in structural investigations of molecular species. In addition, first principles calculations of structure and vibrational properties is of paramount importance in understanding experimental Raman spectra and hence elucidating the nature of structural units. Structural units, representative of the above systems structure, were optimized at CAM-B3LYP/TZVp theoretical level. Raman spectra were interpreted based on the harmonic frequencies and the activities of vibrational modes obtained by the DFT analysis.

Molecular structures consist mainly of ($AsX_{3/2}$) pyramids and ($X\text{-}As\text{-}X_{3/2}$) quasi-tetrahedral units. Their As-X bond lengths and atomic charges have been correlated with chemical environment. The vibrational spectra (Raman and IR) have been recorded and analyzed as they can provide insight about the atomic arrangement over the short- and medium-range structural order. Changes of the Raman spectra reveal that appreciable structural changes take place upon variation of As/X atomic ratio.

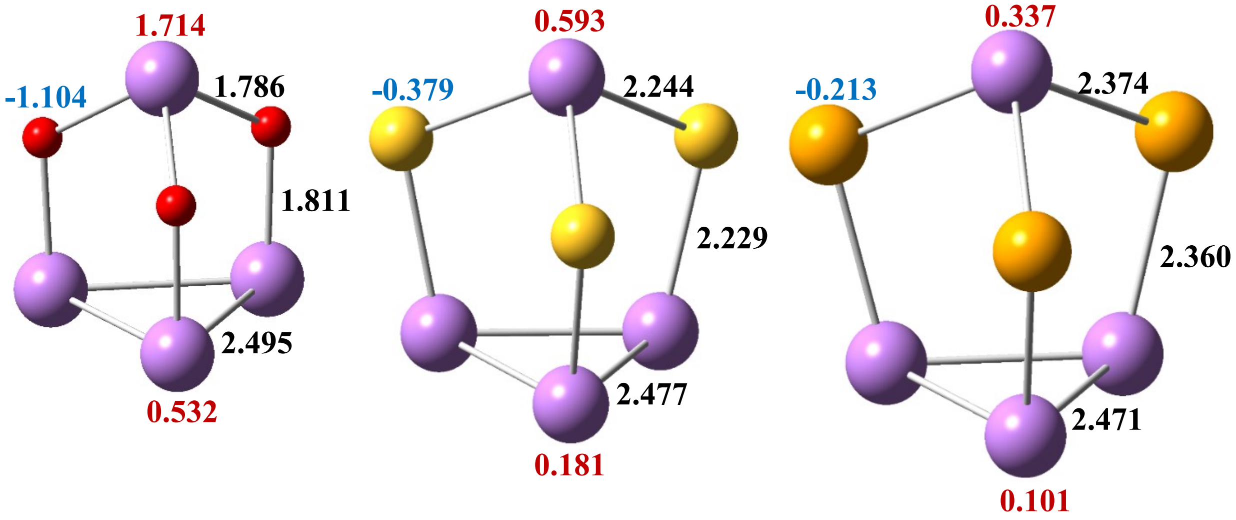

Figure. Ball and stick draws of the CAM-B3LYP/TZVp fully optimized As_4X_3 molecules. Notation for labels: black (bond lengths in [Å]), red (As charge), blue (O, S, Se charge). Notation for atoms: O (red spheres), S (yellow spheres), Se (orange spheres).

Cytotoxic activity against A549 lung cancer cell line of ruthenium-arene-cyclopentadienyl full sandwich complexes.

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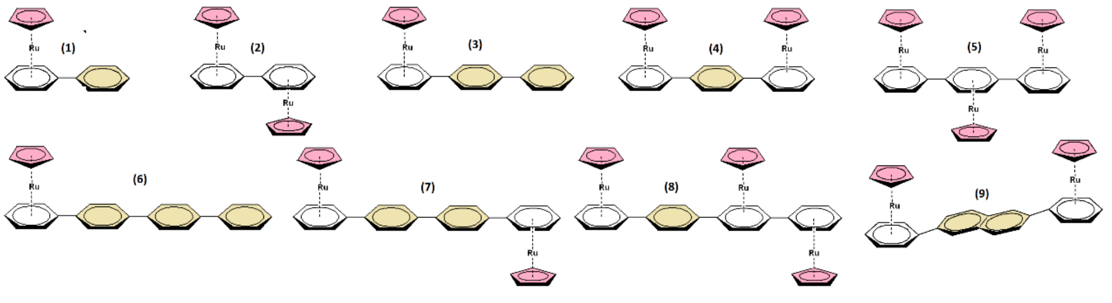
Recent research highlights the significant cytotoxic and selectivity properties of ruthenium arene full sandwich complexes. In parallel, it is established that small η^6-arene derivatives exhibit strong DNA binding affinity [**1**]. Building upon these concepts and aiming to address the solubility challenge of η^6-arene, we synthesized, characterized and investigated the properties of water soluble Ru(II) full sandwich mixed arene cationic complexes. These complexes denoted as $[(\eta^6\text{-arene})\mathrm{Ru}(\eta^5\text{-Cp})_n]^{n+}(\mathrm{PF}_6)_n$, where η arranges from 1 to 3 and η^6-arene is biphenyl, p-terphenyl, p-quaterphenyl and 2,6-biphenyl naphthalene. The above compounds were fully characterized using spectroscopic techniques and single crystal diffraction methods. To evaluate cytotoxic potential, we assessed the effect of complexes (**3**), (**4**), (**6**), (**7**), (**9**) on the lung cancer cell line A549. Impressively, complexes (**6**), (**7**) and (**9**) demonstrated significant cytotoxicity yielding IC$_{50}$ values 17, 65 and 16 μM respectively. In order to establish a relationship between cytotoxicity and DNA binding characteristics, we examined the interactions between the synthesized complexes (**1**)-(**9**) and the DNA duplex d(5′-CGCGAATTCGCG-3′)$_2$ utilizing fluorescence and NMR spectroscopy. Preliminary results revealed that complexes (**2**), (**4**) and (**5**) exhibited low DNA binding affinity while complexes (**1**), (**3**), (**6**), (**7**) and (**9**) displayed a higher affinity.



Acknowledgements: E.S. and T.T were financially supported by the project "Development of research infrastructure for the design, production, development of quality characteristics and safety of agrofoods and functional foods (RI-Agrofoods)" (MIS 5047235) which is implemented under the Action "Reinforcement of the Research and Innovation Infrastructure", funded by the Operational Programme Competitiveness, Entrepreneurship and Innovation (NSRF 2014- 2020) and co-financed by Greece and the European Union (European Regional Development Fund).

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Decontamination of aqueous environments from mercury and organic dyes using polyurea cross-linked calcium alginate aerogels

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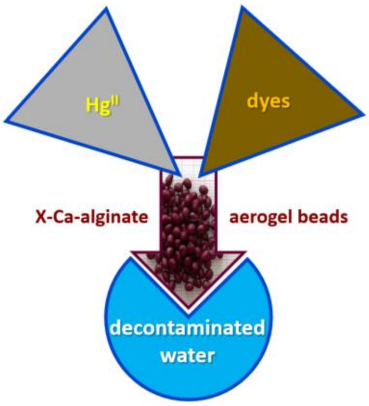
Highly toxic mercury species and organic dyes are classified among the most severe environmental pollutants affecting living organisms and the ecosystem in general. Circulating in the environment for thousands of years, they occur in waters, also affecting both natural and human activities. Since water treatment for the removal of these pollutants is crucial, numerous methods have been developed, such as adsorption, precipitation, flocculation, ion exchange, reverse osmosis, complexation or sequestration, with adsorption being considered as the most appropriate. Various materials have been used, such as carbon- and clay-based adsorbers, organic polymers, metal-organic frameworks (MOFs) or aerogels. In this work, a new class of biopolymer-based aerogels, polyurea-crosslinked calcium alginate (X-Ca-alg) aerogels, were studied in terms of their sorption capacity for Hg^{2+} ions in concentrations encountered in contaminated waters (in the ppb range), as well as for various organic dyes, both cationic and ionic. X-Ca-alg aerogels have a high specific surface area (322 m^2 g^{-1}) and porosity (93% v/v) and are mostly macroporous materials, with portions of mesoporosity and microporosity. Our previous studies have demonstrated that they can adsorb a quite wide range of metals such as lead [1], uranium [2], europium [3], thorium [3] etc. Within the concentration range observed in real contaminated samples (50-180 ppb), Hg^{2+} removal exceeded 85%. Hg^{2+} was also efficiently removed from industrial wastewater (71%). Regarding the organic dyes studied, the sorption capacity of X-Ca-alg aerogels was found equal to 0.054 mol kg^{-1} for methylene blue and 8.4×10^{-3} mol kg^{-1} for crystal violet (from *Langmuir* isotherms), whereas the anionic dyes methyl orange and Congo red were not adsorbed.



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Coordination Clusters Simultaneously Containing 3d and 4d Metal Ions

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Heterometallic coordination clusters have become the focus of interest by many groups around the world due to their involvement in various areas, including Bioinorganic Chemistry, Catalysis, Optics and Molecular Magnetism. Polynuclear 3d/4f coordination clusters have dominated this field in the last 15 years [1]. On the contrary, clusters containing 3d and 4d or 5d metal ions are much less investigated. An important synthetic route is based on one-pot procedures involving a mixture of appropriate 3d- and 4d- metal sources and a primary organic ligand possessing functionalities (coordination "pockets") for preferential binding of the two different transition metal ions, and trying to exploit the HSAB principle. Using the potentially tetradentate ligands saphHCOOH and 4ClsaphHCOOH (Figure, left) we have prepared and characterized a variety of $\{Zn^{II}_4M^{III}_2\}$, $\{Cd^{II}_2M^{III}_2\}$ and $\{Cd^{II}Cr^{III}_2\}$ complexes, where $M^{III} = Cr^{III}$, Fe^{III}. The structures of the complexes were solved by single-crystal X-ray crystallography (Figure, middle) and their study was performed by variable-temperature and variable-field magnetic susceptibilities, as well as various spectroscopic techniques (Figure, right).

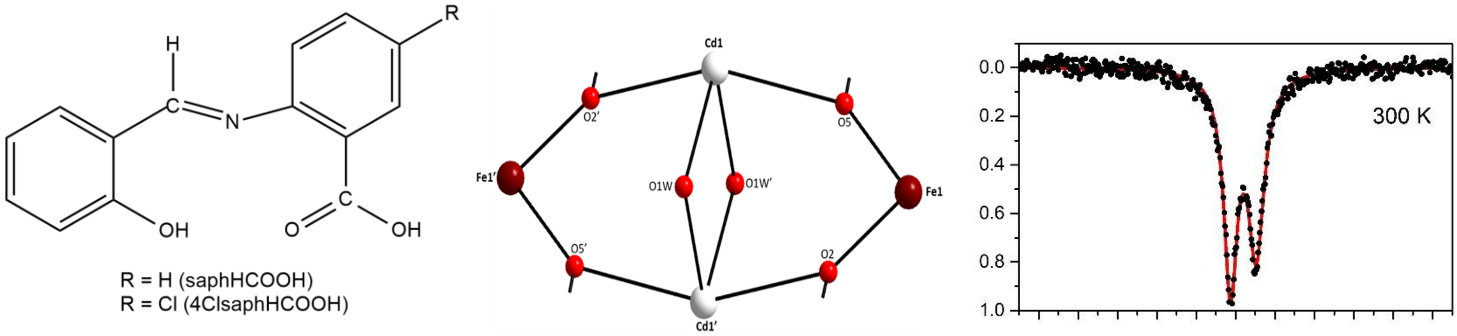

Figure. The ligands used (left), and the core (middle) and ^{57}Fe-Mössbauer spectrum (300 K) of the complex $[Cd^{II}_2Fe^{III}_2(saphCOO)_4(NO_3)_2(H_2O)_2]$.

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Synthetic Entry into Polynuclear Lead-Manganese Chemistry: High Oxidation State Pb/Mn Clusters with Unprecedented Structural Motifs

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Manganese chemistry gathered a lot of interest from the scientific community due to the vital role it played in the development of Single Molecule Magnetism as an exciting research field with a variety of potential technological applications. Even though, in recent years, lanthanide-based Single Molecule Magnets (SMMs) have dominated the field, there is still a case to be made for polynuclear Mn clusters at moderate-to-high oxidation states. SMMs exhibit superparamagnet-like properties, which can also be ascribed to classical magnets, while at the same time they can undergo quantum tunneling of their magnetization, hence acting as nanoscale particles that straddle the boundary between the classical and quantum world.[1] The synthesis of most of these high nuclearity compounds occurs via the self-assembly process, which enables the employment of a second metal ion, and subsequently the possibility to obtain new heterometallic complexes with unprecedented structural motifs and interesting single or multiple physical properties. The {Mn_4Ca} cluster and the $BiMnO_3$ perovskite-type material constitute representative examples of the importance of manganese heterometallic chemistry, with the former involved in the catalytic oxidation of H_2O to O_2 during photosynthesis, and the latter acting as a multiferroic material exhibiting mutually ferromagnetism and ferroelectricity.[2]

In this work, we present our first results from the employment of carboxylate ligands in Mn/Pb oxo cluster chemistry (**Figure 1**) as a means of obtaining nano-sized heterometallic complexes that exhibit interesting magnetic and electrical properties with implications in the fields of molecular magnetism, electronics, photonics, batteries, and related technologies.

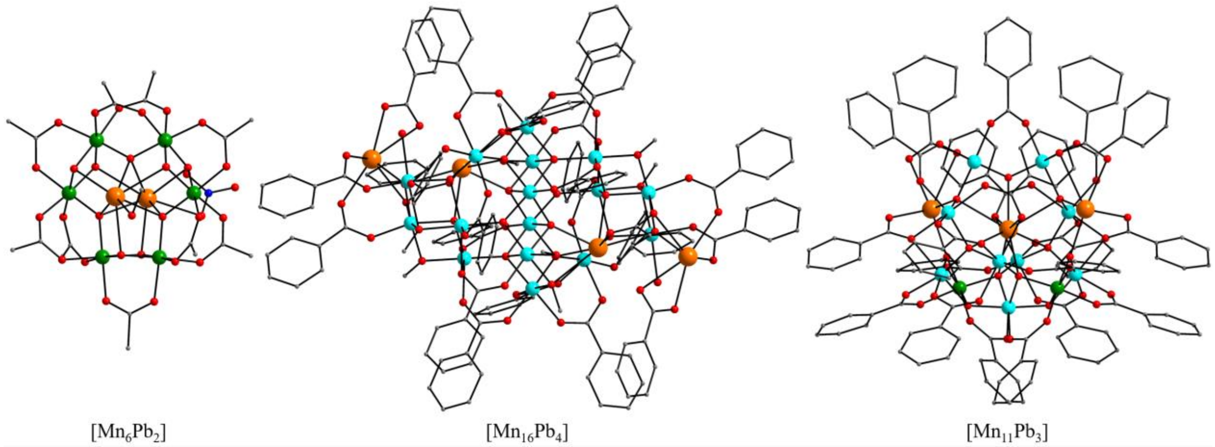

Figure 1. The structures of the heterometallic Mn/Pb complexes discussed in this work.

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The use of manganese oxide minerals from mining waste for energy storage and its electrocatalytic activity for HER

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Natural and synthetic Manganese oxides have a wide range of applications, including metal adsorption, energy storage, rechargeable lithium batteries, and catalysts for electrochemical hydrogen and oxygen evolution reactions. This paper examines the electrochemical behavior of naturally occurring manganese oxides obtained from a manganese ore deposit in northern Greece's Drama region. The samples were selected from abandoned waste piles in the closed mine of Kato Nevrokopi (Drama, Greece).

First, we used natural nsutite (γ-MnO_2) for the preparation of electrodes because nsutite stands out as one of the most promising candidates for applications in energy storage. Additionally, different manganese oxide phases (todorokite..) were subjected to heat treatment at 1000°C for two hours in order to produce hausmannite (Mn_3O_4), which was also tested for its efficiency as an electrode material in our electrochemical experiments.[1] The electrodes were prepared by using natural (γ-MnO_2) and prepared (Mn_3O_4) oxides as paste and carbon black paper. Their electrochemical properties are measured by conducting cyclic voltammetry together with charge-discharge measurements and comparing the results with those from synthetic analogues.[2] Lastly, experiments were carried out to determine whether these materials possess the capability for hydrogen production via the hydrogen evolution reaction.[3] Both electrodes show promising results, although the hausmannite electrode exhibits superior performance equivalent to a supercapacitor.

Acknowledgements

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Nanoparticles with gold, platinum and iron for diagnosis and treatment of glioblastoma

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Glioblastoma multiform (GBM) is the most common and aggressive type of primary brain tumors. Standard care of GBM includes surgery, radiotherapy and pharmacotherapy-usually with temozolomide-, but still the median overall survival is ranging from 14.6 to 20.5 months [1]. Nanotechnology has emerged as a cutting-edge multidisciplinary technology with functional ability in diverse fields, including medicine for the treatment of cancer. Nanoparticles improve the solubility, stability, biodistribution and pharmacokinetic properties of the drug, along with the targeting capacity of specific cells and tissues. Drug delivery systems which emanate from the consolidation of different metals exhibit improved physical and optical properties [2], [3].Herein, we introduce the construction of nanosystems for "theranostic" applications on glioblastoma, which consists of gold coated platinum (Au@Pt) nanoparticles, iron oxide magnetic "nanoflowers" (mNFs) and iron coated platinum (Fe@Pt) nanoparticles. The nanoparticles are evaluated for their structural properties and the colloidal stability through TEM images and DLS measurements, respectively. The nanostructures were biologically evaluated to test their blood compatibility, cellular compatibility in HEK293 and U87MG cell lines and their internalization to the cells through ICP measurements and fluorescent microscopy. Moreover, Flow Cytometry was used to further test their impact on apoptosis and cell cycle and Western Blot to investigate how the nanoparticles influence the pathway of development of glioblastoma cells.

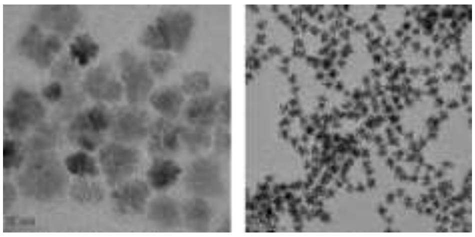

Figure. mNFls, Au@Pt NPs

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Synthesis and Optical Characterization of PbS/CdS Colloidal Quantum Dots emitting at telecommunication wavelength

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Colloidal quantum dots (CQDs) have been attracted considerable attention due to their excellent optoelectronic properties such as tunable band gap and high optical stability. In the visible regime, CQDs materials have already been successfully employed in optoelectronic devices. On the other hand, the burst of near infrared (NIR) technologies such as detectors, face recognition, food monitoring and telecommunication, prerequisites materials emitting at the low energy part of the electromagnetic wavelength. Nevertheless, despite the plethora of semiconductors in visible region, only a few examples exist with a tunable band gap in NIR with lead sulphide (PbS) semiconductor CQDs taking the lead due to the high spectral tunability (500-3000nm). Therefore, here we focus on the synthesis of PbS CQDs emitting at telecommunication wavelengths (1500-1620nm) for lasing applications. The high degeneracy of PbS (8-fold) is the main bottleneck for the realization of low-threshold lasing due to the Auger limited gain. Hence, we synthesised a series of core/shell PbS/CdS CQDs with suppressed Auger rates and tunable band-edge absorption across the telecom spectral window. The epitaxial growth of the CdS shell was achieved via cation exchange reaction producing CQDs of high optical stability, narrow size distribution and low trap state density reaching Auger lifetimes up to 320 ps.

Synthesis, characterization and cytotoxic activity of monofunctional mixed ligand Pt (II) cationic complexes

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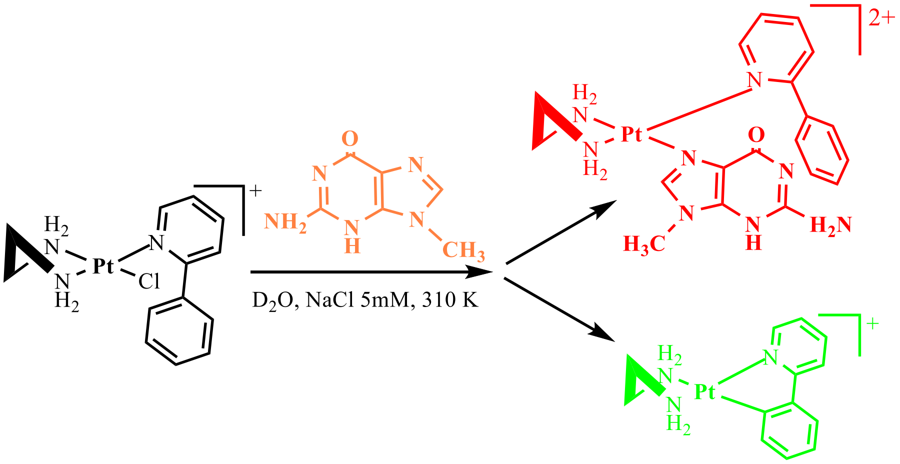
Monofunctional platinum (II) cationic complexes represent a promising category of novel metallodrugs, as they demonstrate enhanced therapeutic efficacy and reduced side effects in cancer chemotherapy. This unique profile stems from their involvement in two principal processes that lead to cytotoxicity. Primarily, these complexes possess the capacity to impede RNA polymerase II activity during transcription by generating monofunctional DNA adducts, thereby inducing double helix distortion through a distinct mechanism compared to classical bifunctional platinum drugs. Secondly, these complexes act as substrates for organic cation transporters (OCTs), thereby influencing the intratumoral distribution of the compound. These characteristics, in conjunction with the steric impact of a bulky substituent which modulates the hydrolysis dynamics of the complex within viable cells, have sparked notable interest in investigating additional monofunctional Pt (II) complexes.[1] In the present research, monofunctional Pt (II) complexes with the general formula of $[Pt(en)(L)Cl]^+$, where en = ethylenediamine and L = pyridine, 2-methylpyridine, 2,6-dimethylpyridine, 2-phenylpyridine, were synthesized, characterized and their hydrolysis kinetics were performed using various NMR techniques. Their cytotoxic potential was also examined in A549 lung cancer cell line. The results reveal significant antiproliferative activity associated with the complex featuring the 2-phenylpyridine ligand. An inquiry into the interaction between this complex and the nucleobase 9-methylguanine was further assumed. The resulting findings supported the formation of a novel complex in a monofunctional pattern, potentially corelated with its corresponding observed activity.



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Synergistic Antimicrobial and Photocatalytic Effects of TiO_2@Ag Nanoparticles

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Titanium dioxide (TiO2) nanoparticles are pivotal in sustainable nanocomposite research, particularly in UV-driven photocatalysis due to their significant surface area, stability, and cost-effective synthesis. [1] Incorporating noble metal nanoparticles can heighten TiO2's photocatalytic ability by improving electron-hole separation and extending absorption into the visible spectrum. [2] Enhancing the antimicrobial behavior of Ag@TiO2 Nps is possible by adding economical antimicrobial molecules like tannic acid (TA), derived from plants. [3]

In this project, spherical TiO_2 nanoparticles were synthesized through a revised sol-gel process, with high yield and monodispersity. For the synthesis of colloidal silver nanoparticles (Ag Nps), a fast and green method was established, where tannic acid acts as both a reducing and capping agent. Hybrid Ag@TiO_2 Nps were fabricated by embedding Ag Nps on the surface of TiO_2 Nps in the presence of TA. The nanocomposites were characterized structurally by FT-IR and XRD, while their morphology was determined by SEM and TEM and colloidal stability was assessed through DLS. The photocatalytic activity was systemically evaluated through UV-Vis spectroscopy by studying the photodegradation of methyl orange (MO), after visible light irradiation. Biological evaluation included biocompatibility assessment on healthy skin cells (HACAT) and antimicrobial activity on gram-negative and gram-positive bacterial strains (E.Coli and St.Aureus).

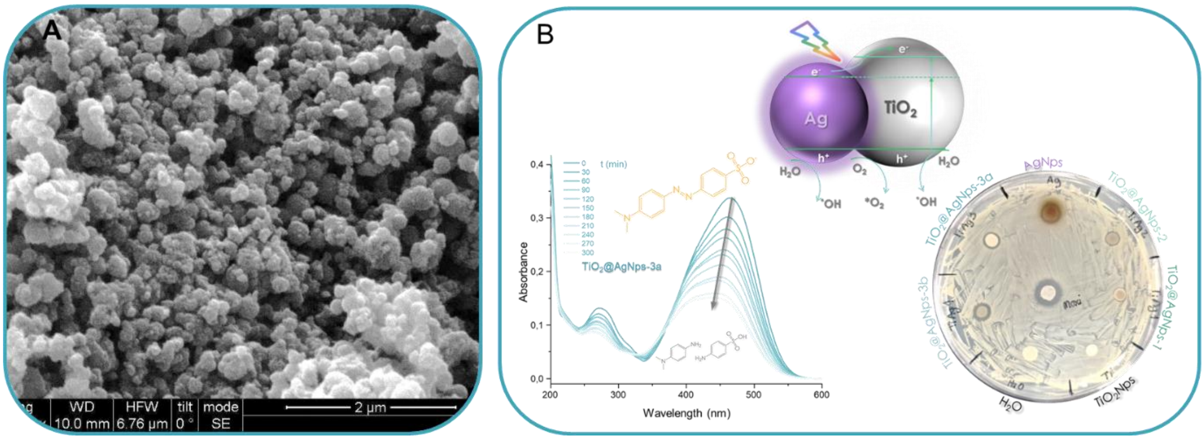

Figure. A) Morphology of Ag@TiO_2 Nps via SEM. B) MO degradation and antimicrobial effect on St. Aureus after visible light irradiation.

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DNA binding interactions of binuclear Ru(II)-arene cytotoxic complexes

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Cancer remains a substantial threat to human life, and there is a significant clinical necessity for anti-cancer drugs. Frequently employed inorganic chemotherapeutics like cisplatin, carboplatin, and oxaliplatin, display specific disadvantages such as notable systemic toxicity and the emergence of drug resistance. Utilizing ruthenium compounds as cytotoxic agents brings forth several advantages over traditional chemotherapy, including minimized side effects and enhanced effectiveness.[1] Exploration of binuclear ruthenium complexes that interact with DNA in a non-coordinative mode offers an alternative way for the development in cancer chemotherapy. Recently, our group reported on the cytotoxicity of novel binuclear ruthenium(II)-arene complexes and their DNA binding properties.[2] The correlation between the binding affinities, the length and the flexibility of the bridging ligands, towards the Dickerson sequence, with their cytotoxic activity against various cancer cell lines was established. Significant specificity towards A2780 and RES A2780 was also noted.[2] Aiming to further our understanding of the binding interactions between this type of complexes and to see if the charge of the complex affects interaction with DNA and cytotoxicity, we synthesized four new binuclear ruthenium-arene complexes. The new complexes differ from the previous ones on the entire charge. This was made possible by engaging the anionic ligand, benzo[h]quinoline (bqn), instead of the neutral 1,10-phenanthroline (phe). As a result, the new binuclear complexes exhibit charge +2 (bqn-bqn) and +3 (phe-bqn) and through the utilization of the same BLs they maintain the structural characteristics of the previous ones (phe-phe). To investigate the impact of charge on the affinity of complexes for DNA, we employed the DNA model d(5′-CGCGCG-3′)$_2$ and determined binding constants using fluorescence spectroscopy. Our results indicated a higher affinity for the DNA is shown by the more positively charged complexes. Also, the increase of the length of the BL at the +2 complexes have a similar effect on the affinity of the complexes for DNA, as it is also observed in the case of +4 complexes. This suggests that the complexes featuring the longest bridging ligand displayed the greatest affinity for the DNA. We also assessed the cytotoxicity of complexes linked by the same BL (4,4’-bipyridine) but different charges, (+2, +3 and +4) against the A549 cancer cell line. Our results indicated that the triple charged complex, $[(\eta^6\text{-cym})\text{Ru(phe)}(\mu\text{-bpy})\ (\text{bqn})\text{Ru}(\eta^6\text{-cym})]^{+3}$ exhibited the highest cytotoxicity with an IC_{50} value at the scale of few μM.

Acknowledgements: D.T. and T.T were financially supported by the project “Development of research infrastructure for the design, production, development of quality characteristics and safety of agrofoods and functional foods (RI-Agrofoods)” (MIS 5047235) which is implemented under the Action “Reinforcement of the Research and Innovation Infrastructure”, funded by the Operational Programme Competitiveness, Entrepreneurship and Innovation (NSRF 2014- 2020) and co-financed by Greece and the European Union (European Regional Development Fund).

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Self-assembly of porphyrin dipeptide conjugates influences the photocatalytic H_2 production efficiency

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Hydrogen can be obtained from water splitting, providing a sustainable alternative to carbon-based fuels, since the only product from its combustion is water. Inspired by nature, scientists are working on the development of artificial photosynthetic systems that can mimic the energy conversion processes of plants and other photosynthetic organisms. In natural photosynthesis, the efficient light harvesting can be largely attributed to the well-organized structures of chlorophyll molecules which are formed, in some cases, via self-assembly process.[1] Therefore, developing highly ordered nanostructures of light-absorbing molecules such as chromophores, researchers aim to enhance the efficiency of solar energy capture and conversion in artificial systems as well. Herein, a dipeptide (Cbz-Ala-Phe-OH) was covalently attached to a porphyrin macrocycle, and the resulting hybrid was able to form different self-assembling nanostructures (spheres, tubes, fibers) using the “good-bad” solvent protocol. This hybrid was found to be an effective solid photosensitizer towards H_2 production. Depending on the nanostructure of the porphyrin-dipeptide conjugate, the catalytic activity varied. The maximum H_2 evolution was obtained with the tubular nanostructures (193,51 μmol of H_2 or 543,47 TON_{CAT}).

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Biological evaluation of TiO_2-based photocatalytic nanoparticles

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In our lab we work on the synthesis of innovative modified nanoparticles based on titanium with increased antipollutant and antimicrobial activity in visible light. Although titanium and titanium alloys are characterized by adequate stability and biocompatibility, their materials lack of intrinsic antibacterial activity.[1] Titanium dioxide (TiO_2, titania) is a compound with risen scientific interest due to its ability of producing ROS under UV light (photoactivity) and inducing cell death.[2] Efforts have been made to conjugate metal nanoparticles with enhanced antibacterial activity to titanium. The different types of photocatalytic nanoparticles synthesized in our lab are constituted of TiO_2@Ag, TiO_2@ZnO, TiO_2@QDs and TiO_2@Cu. Their crystallinity was characterized by PXRD analysis and their morphology and size were studied with SEM and TEM analyses. The present work is focused on the biological evaluation of these nanoparticles. All the biological experiments are carried out using a healthy cell line, HaCaT, which is a human epidermal keratinocyte line. First of all, cell cycle is studied following the PI staining protocol. Then, the degree of apoptosis and necrosis caused by the administration of the nanoparticles to the cells is studied following the Annexin V/FITC – 7AAD protocol. Finally, the intracellular production of ROS is studied following the H_2DCF-DA staining protocol.

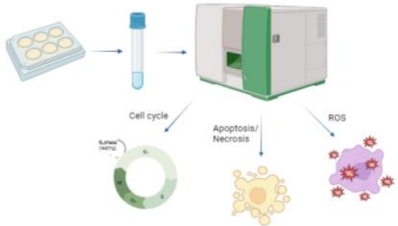

Figure. Procedure for the analyses of cell cycle, apoptosis/necrosis and ROS production.

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Acknowledgements: This research is co-financed by Greece and the European Union (European Social Fund – ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning 2014 – 2020» in the context of the project “Innovative Titanium Nanoparticles for Development of Autocleaning and Auto antibacterial Application” (MIS 5131364, TiClean).

Synthesis, characterization and biological evaluation of bimetallic hybrid Iron/Europium nanoparticles

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The purpose of this work was to synthesize, characterize, structurally and morphologically, the bimetallic hybrid Iron/Europium nanoparticles as well as to evaluate them biologically. The compositions were carried out through the co – precipitation method and contained the synthesis of magnetic iron oxide nanoparticles coated with citrate and europium in different ratios of Fe:Eu (1:3, 1:1, 1:0.25). For the morphological characterization of the nanoparticles, different techniques were carried out. UV – Vis and DLS data showed that increasing the amount of europium added resulted in nanoparticles of irregular size, while their tendency to form agglomerates is high. Z – potential results showed that the nanoparticles with Fe:Eu ratio 1:1 have the best colloidal stability.[1] FT – IR results confirmed the formation of magnetite, the binding of the citrate to the magnetite’s surface and the formation of europium oxide on the surface of citrate, especially in the cases of nanoparticles with ratios of Fe:Eu 1:3 and 1:1. PXRD confirmed the formation of magnetite in all the compositions and the presence of europium hydroxide rods in the nanoparticles with Fe:Eu ratios 1:3 and 1:1.[2] Biologically, according to MTT and the wound healing assay results, it was concluded that the synthesized nanoparticles were only a little toxic for the healthy cells reducing their reproductive capacity, whereas the nanoparticles with Fe:Eu ratio 1:3 showed the best anticancer activity.

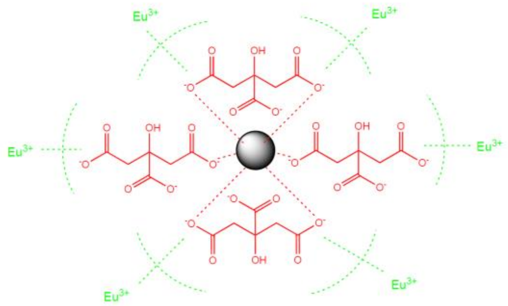

Figure. Structure of iron oxide magnetic nanoparticles coated with citrate and europium.

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Structural and EPR properties of Cu(II) complexes bearing $\{Ph_2P(O)NP(O)Ph_2\}^-$ and 2,2′-bipyridine as ligands

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Only a handful of Cu(II) complexes bearing chalcogenated imidodiphosphinato type of ligands $\{Ph_2P(E)NP(E)Ph_2\}^-$, E = O, S, have been reported up to now.[1-3] In this work, the synthesis, as well as the structural and spectroscopic characterization of $[Cu\{Ph_2P(O)NP(O)Ph_2\}(2,2'\text{-bipyridine})(X)]$, X = NO_3^- (**1**), I^- (**2**), PF_6^- (**3**), will be presented. X-ray crystallographic studies revealed that complexes **1**, **2** and **3** exhibit trigonal bipyramidal CuO_3N_2, square pyramidal CuO_2N_2I and square planar CuO_2N_2 first coordination spheres, respectively (Fig. 1). UV-vis and cw EPR spectroscopy studies provided evidence that, in solution, all three complexes exhibit similar tetragonal structures. Furthermore, ligand super-hyperfine interactions of the unpaired electron of complexes **1** and **2** were investigated by ENDOR and HYSCORE spectroscopies.

Acknowledgments. We would like to thank the Special Account for Research Grants of the National and Kapodistrian University of Athens for financial support.

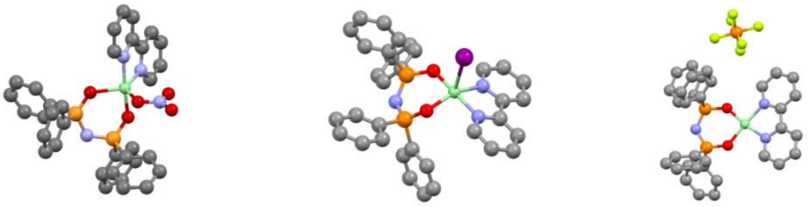

Figure 1: Molecular structure of complexes **1** (left), **2** (middle) and **3** (right).
Color coding: Cu (green), O (red), N (blue), P (yellow), C (grey).

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The Impact of Cu Concentration on the Optical Attributes of TiO_2 Nanoparticles and Evaluation of the Nanohybrids' Solar-Light Driven Water Splitting Efficacy for Green Hydrogen Evolution

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Photocatalytic water splitting is a promising and sustainable approach to harness solar energy and produce clean hydrogen fuel. Titanium dioxide (TiO_2) nanoparticles, due to their exceptional photocatalytic properties and chemical stability, have been extensively studied in this context [1]. Moreover, the positioning of the Valence Band (VB) and Conduction Band (CB) of TiO_2, with a VB potential of approximately +2.9 V vs NHE and a CB potential of approximately -0.3 V vs NHE, is ideally suited for the half reaction of H_2 evolution from water at a neutral pH, making it a crucial component for this sustainable process. However, the intrinsic wide bandgap of TiO_2 limits its light absorption to the ultraviolet (UV) region, rendering it less efficient for solar-driven reactions [2]. In this study, different dopant concentrations of copper were systematically investigated to select the catalyst with the optimal copper loading. This thorough exploration allows us to identify the Cu-TiO_2 nanomaterial that exhibits the highest photocatalytic performance for hydrogen evolution from water under solar light irradiation. The structural and morphological characterization of the as-made nanoparticles employed several techniques, including powder X-ray diffraction (pXRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS) in reflectance mode was used for the optical characterization of the nanocomposites. Kubelka-Munk plots were generated to calculate the indirect bandgap and the Urbach energy of each nanocomposite.

To assess the photocatalytic activity of the modified nanoparticles, a Xenon (Xe) lamp simulating full solar light irradiation was utilized. Different filters were employed to identify the absorption edge that initiates the photocatalytic reaction.

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Assessment of Fracture Toughness in Cementitious Graphene Nanocomposites via Electrical Impedance Analysis

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The present work investigates experimentally the improvement of fracture toughness and electrical conductivity in the hardened cementitious matrix after the addition of graphene nanoplatelets (GnPs), at four different concentrations varying between 0.05 wt% and 0.4 wt% per cement. The experimental investigation is conducted through flexural and electrical impedance spectroscopy (EIS) tests on prismatic specimens. The study is oriented towards establishing a correlation between the electrical response of the nanocomposites under alternate current and the exhibited fracture toughness values (K_{Ic}). The flexural test results show that the incorporation of the GnPs in the matrix can increase the average K_{Ic} values and can decrease the average resistivity (ρ) when compared with the reference matrix. The maximum increase in K_{Ic} (+ 29 %), and the decrease in ρ (- 68 %) were found in the mixture with the lowest amount (0.05 wt%) of GnPs. Moreover, the comparison of the ρ values and the K_{Ic} values, as a function of the GnPs concentration, reveals a reverse relation between the two parameters (K_{Ic} and ρ). The functional correlation between these parameters was also confirmed by linear regression analysis, resulting from the experimental data fitting. The analysis provides evidence that EIS can be used as a non-destructive tool to assess the fracture toughness of cementitious nanocomposites.

In this study, the enhancement of fracture toughness and electrical conductivity are explored within a hardened cementitious matrix following the incorporation of graphene nanoplatelets (GnPs) at concentrations ranging from 0.05 wt% to 0.4 wt% per cement weight. The study is oriented towards establishing a correlation between the electrical behaviour of the nanocomposites under alternate current and the exhibited fracture toughness values (K_{IC}).

The flexural tests results indicate that the inclusion of GnPs in the matrix can yield increased average K_{IC} values and reduced average resistivity (ρ) when compared to the reference matrix. Notably, the most significant improvements in K_{IC} (+29%) and reduction in ρ (-68%) were observed in the mixture with the lowest GnPs concentration (0.05 wt%). Furthermore, the analysis of ρ values and K_{IC} values as a function of GnPs concentration reveals an inverse relationship between these two parameters. This functional correlation was further confirmed through linear regression analysis, based on the experimental data fitting.

The results of our study provide compelling evidence that EIS can serve as a non-destructive tool for evaluating the fracture toughness of cementitious nanocomposites. This work contributes to a deeper understanding of the synergy between electrical properties and mechanical performance in these advanced materials, paving the way for innovative applications in construction and structural engineering.

Acknowledgements

The authors gratefully acknowledge funding from the Research e-Infrastructure "Interregional Digital Transformation for Culture and Tourism in Aegean Archipelagos" (Acronym: e-CulTour) {Code Number MIS 5047046} project, which is implemented within the framework of the "Regional Excellence" [Partnership Agreement 2014–2020] of the University of the Aegean, Greece.

Sterics to control metal-arene interactions

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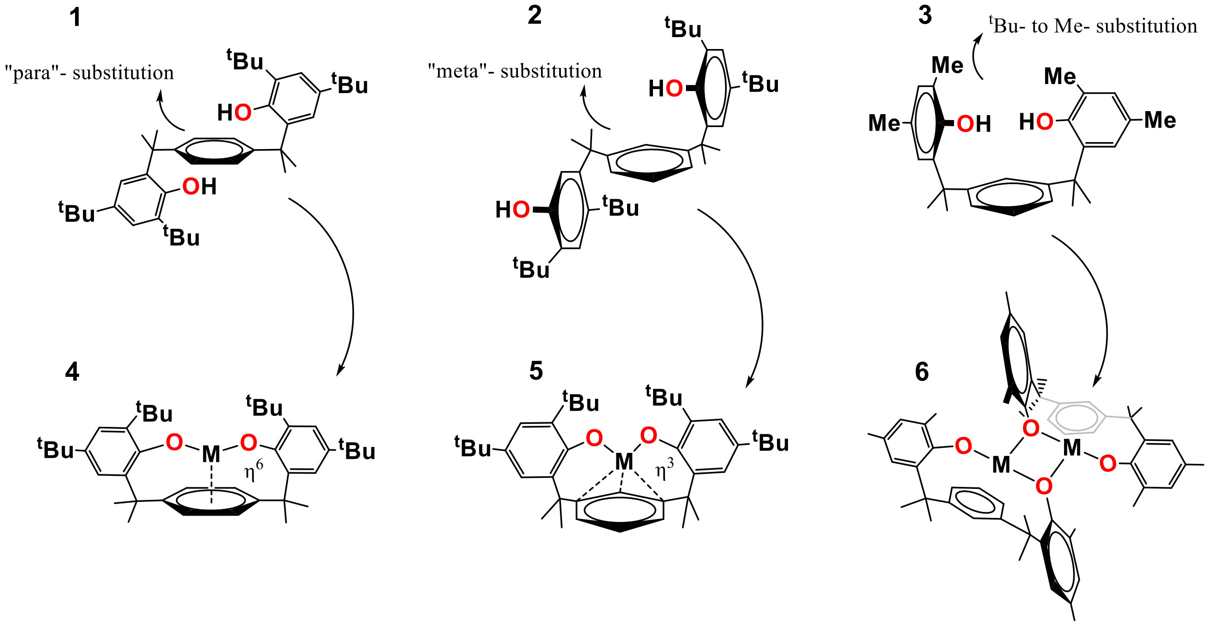
Wanting to design a redox active ligand suitable to support novel electrocatalysts, we synthesized three new bis-phenoxide ligands(**1**, **2** & **3**, see Sch. 1). All of them have the same potential donor properties(L_3X_2 donors) , while the central arene can act as an electron reservoir through metal-arene π-interaction. The latter poses to be key characteristic in electrocatalysis[1]. Steric differences on the framework of the ligands seem to control the coordination result to divalent 3d-transition metals, altering the coordination manner of the central arene.



Scheme 1: Ligands **1**, **2** and **3** have the same donor atoms but differences in the steric bulk of the ligand framework. Protonolysis reactions with the appropriate metal source leads to the formation of the corresponding complexes **4**,**5** and **6**

Using theses ligands, three Fe and three Co complexes were synthesized and characterized structurally and spectroscopically. Preliminary DFT studies were also conducted. Having in hand η^6- , η^3- and dimers with no metal arene interaction, the next step is to perform electrocatalytic experiments to evaluate the role of the metal-arene interaction in various electrochemical transformations.

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Synthesis and characterization of novel polyurea-crosslinked alginate aerogels for antibacterial applications

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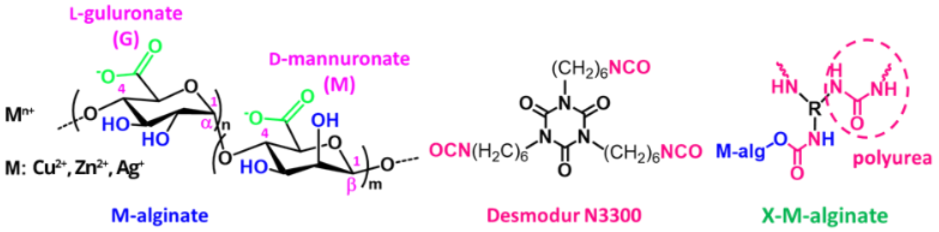
Alginates are natural water-soluble polysaccharides obtained from brown algae. They are linear block copolymers of two diastereomeric monomers, *β*-(1→4)-linked *D*-mannuronic acid (M) and *α*-(1→4)-linked *L*-guluronic acid (G). Alginate aerogels are among the most well-studied biopolymer aerogels, as they can incorporate a great variety of metal cations. Their synthesis is simple, inexpensive and environmentally friendly, as it takes place in water. Also, they are biocompatible and biodegradable, and they have found several applications, including a wide range of biomedical applications. Their main disadvantage is that they are mechanically weak materials and extremely hydrophilic. This has been rectified recently, by applying the X-aerogel technology, initially developed for silica and other inorganic aerogels, in order to prepare polyurea-crosslinked alginate (X-alginate) aerogels [1], via the reaction of pre-formed alginate networks with polyisocyanates introduced, post-gelation, to the pores of the wet-gel via diffusion. Crosslinking with polyurea has proven to be an efficient way to increase the mechanical strength and the stability of alginate aerogels, improving therefore their application potential. For example, X-Ca-alginate aerogels have been found suitable for tissue scaffolding [2]. In this work, analogous new X-M-alginate (M: Cu, Zn, Ag) aerogels have been prepared and they have been tested towards potential antibacterial activity against the Gram-positive bacterium, *S. aureus*. The new X-M-alginate aerogels have bulk densities in the range of 0.2-0.5 g cm^{-3} and BET surface areas in the range of 30-120 m^2 g^{-1}. They seem to have a bacteriostatic activity, with X-Ag-Alg being the most promising materials for this specific application.



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Acknowledgements: This publication is based upon work from COST Action "Advanced Engineering of AeroGels for Environment and Life Sciences" (AERoGELS, ref. CA18125), supported by COST (European Cooperation in Science and Technology). Financial support from the Special Account of Research Grants of the National and Kapodistrian University of Athens is gratefully acknowledged. Covestro AG is also acknowledged for the generous supply of Desmodur N3000.

P_61

Spin Heterogeneity of the S oxidation States of the Oxygen Evolving Complex of Photosystem II

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The light-driven water oxidation to molecular oxygen is a fundamental physicochemical process that takes place during the primary steps of photosynthesis by photosystem II (PSII), a multi-subunit membrane-protein. PSII utilizes solar energy to split two water molecules into molecular oxygen and protons (Figure). The active unit of PSII that catalyzes the oxidation of water is known as Oxygen-Evolving Complex (OEC) and contains an oxygen-bridged Mn_4Ca cluster. During the catalytic cycle the OEC cycles through five oxidation states, S_0-S_1,…S_4-S_0, known as S-state transitions. The O_2 release takes place during the S_3-[S_4]-S_0 transition.

Low temperature EPR spectroscopy has been extensively applied in the study of individual S oxidation states of the OEC. We present a detailed investigation of the EPR spectra of the various S states of OEC in PSII preparations isolated from *Spinacia Oleracea.* The simulations of the EPR spectra reveal Spin heterogeneity of the S states of the Mn_4Ca which correspond to its different geometrical configurations [1,2]

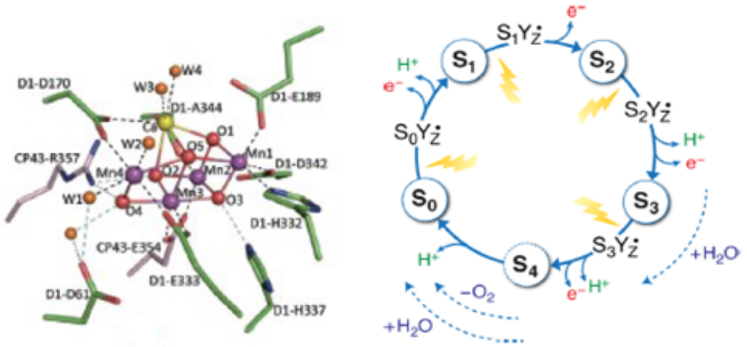

Figure. Left: The Mn_4Ca cluster of Photosystem II, Right: The S oxidation states of Mn_4Ca cluster

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Towards the development of Mn^{III} SCO systems based on N_4O_2 Schiff base organic linkages

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The development of molecular materials with bistable properties, especially for application in information storage, is a constant high-challenge/high-gain goal. In particular, an appealing class of molecular switchable materials are those based on the well-known phenomenon of Spin-Crossover (SCO), where the switching process between the high-spin (HS) and low-spin (LS) states in specific 3d coordination complexes is induced by external perturbations.[1] Although SCO is theoretically possible for octahedral d^4-d^7 metal ions, it is commonly observed in Fe^{II} and Fe^{III} complexes. This fact illustrates its delicate nature due to the synergetic effect of ligand-field strength, ionic charge, and d-electron count. In this context, spin transitions in octahedral d^4 systems, including Mn^{III} and Cr^{II} complexes, are rare and considered exceptional.[2] Schiff base ligands that can generate a N_4O_2 coordination sphere are known to promote ligand fields close to the crossover value.

Herein, we will present our preliminary results concerning our on-going attempts towards the isolation of new Mn^{III} SCO systems based on a new N_4O_2 Schiff base organic linkage (Fig. 1). The successful in-situ Schiff base condensation was supported by vibrational spectroscopy (IR and Raman), while magnetic susceptibility measurements and temperature-dependent Raman spectroscopy were applied to identify the potential occurrence of SCO effect.

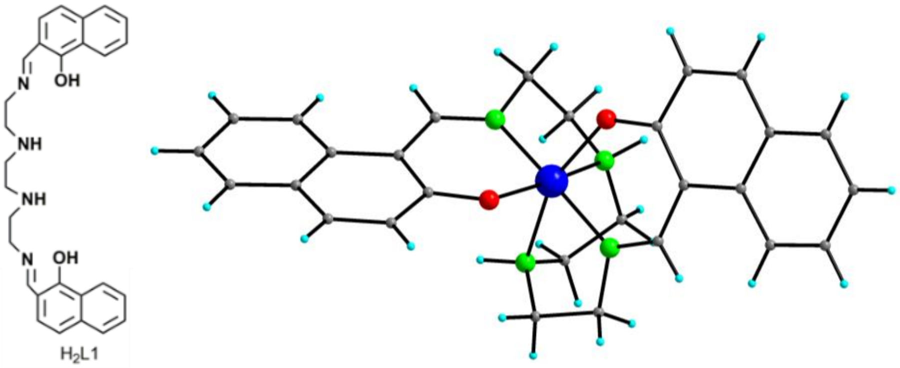

Figure 1. (left) The in-situ generated Schiff base ligand (H_2L^1) used in this work, and (right) the molecular structure of the cation of complex $[Mn^{III}(L^1)](ClO_4)$. Color code: Mn, blue; O, red; N, green; C, gray; H, cyan.

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Tailoring the properties of perovskite oxide materials towards the development of bi-functional cathodes for solid oxide cells applications

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Abstract

The need for the minimization of greenhouse gas emissions, along with the necessity for the de-carbonization of the heavy industry and transportation sectors, has generated an urgent requirement for a shift towards more ecologically sustainable and environmentally conscious substitute fuels and feedstock chemicals. A solution presented by solid oxide electrolytic cells and fuel cells (SOECs and SOFCs) poses as an appealing strategy for recapturing CO_2 emissions. Renowned for their efficiency in comparison to other materials that operate under demanding conditions (high temperatures, reactive gases), SOECs and SOFCs are of great significance for applications in the *power-to-X* decarbonization strategy. Our objective involves the preparation of perovskite materials with modifications in A- and/or B-site, which affect the properties of the resulting perovskite oxide material in terms of stability in redox reactions and ionic and electronic conduction.

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Theoretical and Experimental perspectives on Cu complexes bearing remote N-Heterocyclic Carbene ligands

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N-heterocyclic carbenes today rank among the most powerful tools in synthetic and catalytic chemistry [1], however functionalised NHC's are not so frequently studied. Functionalised NHC's often bring about additional properties of considerable impact in structural chemistry, catalysis, medicine, etc. N-heterocyclic remote-substituted imidazol-2-ylidenes r(NHCs), with heteroatom substituents at the 4- and/or 5-positions of the heterocycle (denoted as r(substituent)) have different nucleophilicity and donor properties, due to the inductive and mesomeric effects of the remote substituent [2].

We are interested in the organometallic chemistry of the r(NH*R*)/r(N^-*R*) ligand couple, existing in equilibrating, tautomeric forms, in solution (fig.1), where *R* is an alkyl or aryl group. We have synthesised and characterised (spectroscopically and crystallographically) a range of copper complexes containing the above-mentioned ligands (fig.2).

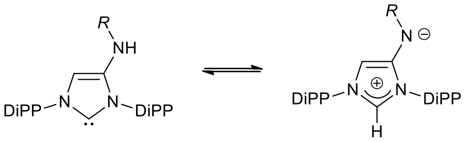

Figure 1: The tautomeric equilibrium of the r(NH*R*) ligand, where R = *t*Bu, DiPP, Cy

Moreover, we have used Density Functional Theory level, to shed light on the electronic structure of such complexes and investigate their photophysical properties (fig.2). The research aims at reaching design principles for future photophysical applications, such as LEDs or TADF emitters [3].

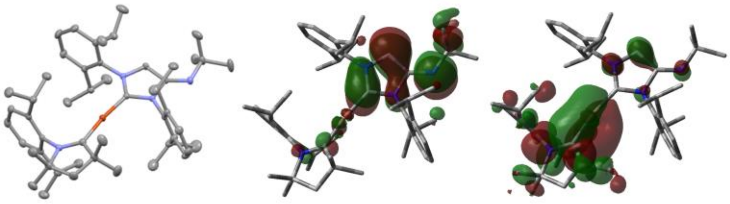

Figure 2: The example of [Cu(^{Me}CAAC)(rN^-*t*Bu)]. The left is obtained from XRD. Middle and right show the HOMO and LUMO, respectively, obtained from DFT (B3LYP/6-31G**).

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pH-sensitive Gold Nanorods for Non-Steroidal Anti-Inflammatory Drugs (NSAIDs) Delivery and DNA-binding studies

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A facile experimental protocol for the synthesis of poly(ethylene glycol) modified (PEGylated) gold nanorods (AuNRs@PEG) is presented as well as an effective drug loading procedure using non-steroidal anti-inflammatory drug (NSAID) naproxen (NAP). The interaction of AuNRs@PEG and drug loaded AuNRs (AuNRs@PEG@NAP) with calf-thymus DNA was studied at diverse temperature revealing different interaction modes; AuNRs@PEG may interact *via* groove-binding and AuNRs@PEG@NAP may intercalate to DNA-bases. The cleavage activity of the gold nanoparticles for supercoiled circular pBR322 plasmid DNA was studied by gel electrophoresis while their affinity for human and bovine serum albumins was also evaluated. Drug-release studies revealed a pH-sensitive behavior with a release up to a maximum of 24% and 33% NAP within the first 180 min at pH=4.2 and 6.8, respectively. The cytotoxicity of AuNRs@PEG and AuNRs@PEG@NAP was evaluated against MCF-7 and MDA-MB-231 breast cancer cell lines. Having in mind that the development of AuNRs as efficient non-steroidal anti-inflammatory drugs (NSAIDs) delivery systems for chemotherapy purposes is still in its infancy, the present work can shed plenty of light and inspire other research groups to work in this direction.

Synthesis and Characterization of Copper doped TiO_2 Nanoparticles with Improved Visible-Light induced Photocatalytic and Antibacterial Performance

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Titanium dioxide (TiO_2) nanoparticles are widely studied due to their photocatalytic properties and chemical stability [1]. The most photocatalytically active form of TiO_2 is anatase; however, it exhibits a relatively large bandgap (3.2-3.3 eV). This feature limits its light absorption capacity in the UV region of the light spectrum. One of the most prominent methods to lower the bandgap of TiO_2 and enhance its photocatalytic ability in visible light is the introduction of metal ions into the TiO_2 crystal lattice during the synthetic procedure. As a result, additional states are created inside the bandgap of anatase TiO_2, extending its absorption into the visible light spectrum. Additionally, modified TiO_2 has enhanced photocatalytic properties due to the reduction of the charge recombination rate. Limited recombination of charges can improve the antifouling and antibacterial properties of the nanocomposites under visible light irradiation [2]. In this study, we report the synthesis of copper-doped TiO_2 nanoparticles through a low-cost and eco-friendly synthetic procedure. The concentration of Cu dopant was varied from 3 to 5 mol% to determine the optimum concentration for the final nanocomposite. Bare TiO_2 nanoparticles were synthesized using the same procedure and served as a reference. Various analytical techniques, including XRD, microRaman IR-ATR, UV-Vis DRS, TEM, and SEM-EDX, were employed for characterizing the doped and undoped TiO_2 nanoparticles. The photocatalytic activity of the synthesized nanocomposites was measured by the degradation rate of organic pollutants, such as Methylene Blue, under low-energy LED lamp irradiation. Their antibacterial activity against E. coli and S. aureus was evaluated under visible light irradiation and in the dark. Finally, their toxicity on human cells was assessed using MTT assays.

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Reactivity Towards Ethylene (Oligo-)Polymerisation Catalysis Reactions of Cr, Fe, Co, Ni Complexes Containing a Novel Pincer CNC-type Ligand with 6 membered N-Heterocyclic Carbenes

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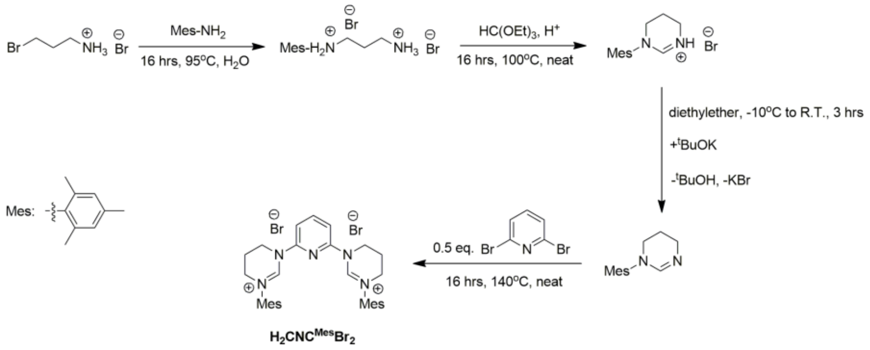
A novel potentially pincer CNC-type ligand salt precursor was synthesised (**Scheme 1**).



Scheme 1: Synthesis of the potentially pincer CNC-type ligand salt precursor.

In situ deprotonation of the salt precursor **$H_2CNC^{Mes}Br_2$** by a strong base and concomitant reaction with suitable metal precursors or direct utilisation of metal precursors with an incorporated intrinsic/internal base, afforded the anticipated pincer complexes (**Figure 1**). All complexes were experimentally explored as candidates for ethylene (oligo-)polymerisation.

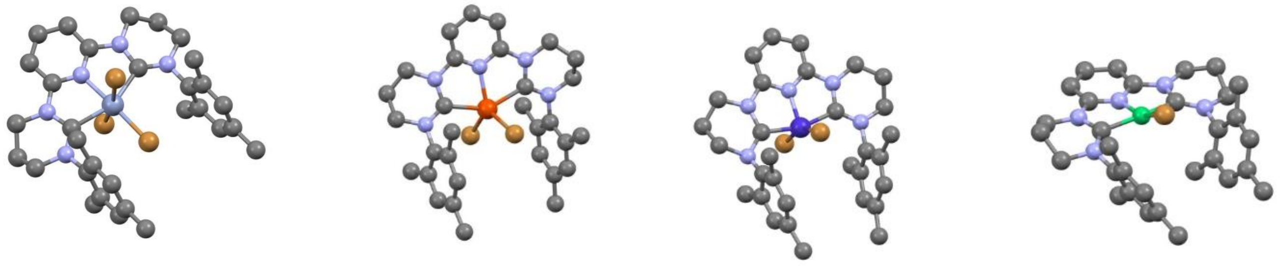


Figure 1: Crystal structures of complexes $CrCNC^{Mes}Br_3$, $FeCNC^{Mes}Br_2$, $CoCNC^{Mes}Br_2$ and $[NiCNC^{Mes}Br]^+$ (from left to right).

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Silver(I) Complexes with 2-pyridyl Oximes and Benzotriazoles as Ligands: Synthetic, Structural and Antibacterial Studies

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Silver has long been known to humans not only as one of the seven metals of antiquity, but also for its antimicrobial properties. With the existence of multidrug-resistant bacteria, the search for new effective strategies has revived the interest in silver [1]. This is due to its high toxicity to microorganisms, while the harmful effects to mammalian cells are not severe. Silver is applied either in the neutral form of nanoparticles or as a cation in salts and coordination complexes. Both forms possess antiviral, antifungal and antibacterial effects, and its mechanisms of bacteriostatic and bactericidal effects are intensely studied. In our poster presentation, we shall describe the syntheses, spectroscopic characterization and structural study of a series of Ag(I) complexes with 2-pyridyl oximes, (py)(R)CNOH, and benzotriazoles, R´btaR´´, as primary organic ligands. The complexes have the general formulae [Ag{(py)(R)CNOH}$_2$]X and [Ag{R´btaR´´}$_2$X], where X^- = NO_3^-, ClO_4^- and $CF_3SO_3^-$, with distorted square planar and trigonal planar structures, respectively. The antimicrobial potency of [Ag(phpaoH)$_2$](NO_3) (R = Ph), [Ag(Mebta)$_2$(O_3SCF_3)] (R´ = H, R´´ = Me) and their corresponding free organic ligands were evaluated against Gram negative and Gram positive microbes, through evaluation of the MIC and MBC parameters. The free ligand shows no activity, whereas the complexes exhibit their strongest activity towards the Gram negative bacterial strain of *P. aeruginosa*. Our results will be critically discussed.

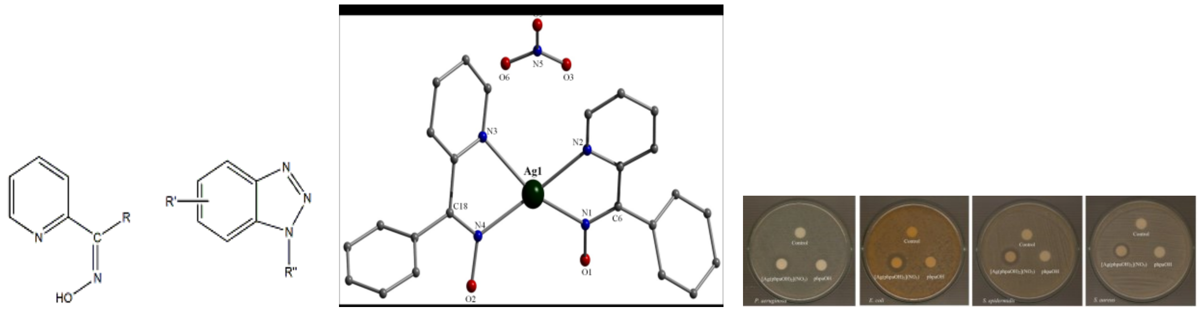

Figure. The ligand used, the molecular structure of [Ag(phpaoH)$_2$](NO_3) and its antimicrobial properties.

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