Foreword

The mission of Centro de Química Estrutural (CQE) a research unit of IST - University of Lisbon, is to contribute to the progress of society by providing top quality Research, Development and Innovation activities in diverse areas of Chemistry, and also to strongly support teaching activities.

The recent enlarged CQE, involving ~110 integrated members (academics and researchers) envisages a broadening of activities with the inclusion of new and complementary scientific and technological valences. The gathering of synergies, the sharing of skills, resources and facilities, and the strengthening of funding opportunities, thus contributing to the international competitiveness of the scientific and technological Portuguese system are our main goal.

We believe that the increased critical mass will enable CQE to gather national and international collaborations, to boost the cooperation with the industrial sector, leading to relevant projects within the Horizon 2020 in crucial areas such as: Development of Novel Catalysts, Ionic and Task-Specific Fluids, Functional Materials and Design, Synthesis, Evaluation of activity and toxicity of Bioactive Molecules up to the start of Clinical Trials

Overall the members of the new team published 291 ISI articles in 2013, and 235 till the 15th September 2014. We include herein a selection of the finest work done by CQE members during such a period. A number of these result from recent established collaborations among the new CQE members and demonstrate the high quality of the work produced.

João Costa Pessoa and Armando Pombeiro
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Synthesis and Catalysis
Polynuclear Copper(II) Complexes as Catalysts for the Peroxidative Oxidation of Cyclohexane in Room Temperature Ionic Liquid Medium


The reaction of copper(II) nitrate hydrate with sodium 2-[2-(2,4-dioxopentan-3-ylidene)hydrazinyl]terephthalate (Na₂HL⁺) in the absence or presence of imidazole (im) leads to the new complexes \[\text{[H}_2\text{O}]\text{Cu}_{0.5}\{\mu-\text{L}^1\text{-}1\kappa\text{O}:2\kappa^2\text{N},\text{O}^\prime\text{O}^\prime\}\text{Cu(H}_2\text{O)}\text{]\}; (1) and \[\text{[Cu}(\text{im})\{\mu-\text{H}^\text{L}^1\text{-}1\kappa\text{O}:2\kappa^3\text{N},\text{O},\text{O}'\}\text{]_2}\] (2), respectively, whereas the 1D coordination polymer \[\text{[Cu}_2(\text{H}_2\text{O)}_2\{\mu-\text{H}^\text{L}^2\text{-}1\kappa^3\text{N},\text{O},\text{O}':2\text{κO}^\prime\}\{\mu-\text{L}^2\text{-}1\kappa^2\text{N},\text{O},\text{O}':2\kappa^2\text{N}^\prime,\text{O}^\prime\}\text{]}\] (3) is obtained from Cu(NO₃)₂·2·5H₂O and sodium 2-[2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl]terephthalate (Na₂HL²). All of the compounds were characterized by ESI-MS, IR spectroscopy, elemental analysis and X-ray diffraction analysis. Di- or tri-deprotonated ligands display different coordination modes and lead to distinct nuclearities of the Cu²⁺ complexes depending on the conditions used for the syntheses. Complexes 1–3 were successfully tested as dual-role catalysts for cyclohexane oxidation under acid-free conditions in the ionic liquid [1-butyl-3-methylimidazolium tetrafluoroborate, (bmim)(BF₄)] as well as in acetonitrile. The application of the ionic liquid (IL) increased the product yield and turnover number and decreased the reaction time, in comparison with those for the use of the conventional acetonitrile solvent. Easy recycling of the catalyst, with preservation of almost the initial activity and selectivity, was also achieved by using the IL medium.

ADC-Metal Complexes as Effective Catalysts for Hydrosilylation of Alkynes


Aminocarbene complexes cis-[PtCl₂\{C(N(H))N = CR₂(R₂)=N(H)R1\}CN(R₁)\}] (7–15) prepared via the nucleophilic addition of hydrazones H₂N–N=CR₂R₂ [R₂, R₂ = Ph 4; R₂/R₂ = 9H-fluoren-5; R₂ = H, R₃ = 2-(OH)C₆H₄] to cis-[PtCl₂(CN(R₁))₂] [R₁ = cyclohexyl (Cy) 1, 2,6-Me₂C₆H₃ (Xyl) 2, 2-Cl-6-MeC₆H₃3] were evaluated as catalysts for the hydrosilylation of terminal alkynes with trisubstituted silanes giving vinyl silanes. The optimized catalytic system runs at 80–100 °C in dry toluene for 3–6 h with a typical catalyst loading of 0.1 mol%. A range of substrates with different steric hindrance and activity (Et₃SiH, Pr₃SiH, iPr₃SiH, and...
PhMe₂SiH as silanes; PhCCH, tBuCCH, and 4-(tBu)C₆H₄CCH as alkynes) were successfully transformed into the target silylated products in 83–99% yields attesting the versatility of our catalytic system. Decreasing the catalyst loading to 10–3 mol% guaranteed the maximum TONs of 4.0 × 10⁴ and TOFs of 1.7 × 10⁵ (h⁻¹) that were accomplished within 24 h of the reaction.


**COOPERATIVE METAL-LIGAND ASSISTED E/Z ISOMERIZATION AND CYANO ACTIVATION AT CuI AND CoII COMPLEXES OF ARYLHYDRAZONES OF ACTIVE METHYLENE NITRILES**


New (E/Z)-2-(2-(1-cyano-2-methoxy-2-oxoethylidene)hydrazinyl)benzoic acid (H₂L₄) and known sodium 2-(2-(dicyanomethylene)hydrazinyl)benzenesulfonate (NaHL₁), 2-(2-(dicyanomethylene)hydrazinyl)benzoic acid (H₂L₂) and sodium (E/Z)-2-(2-(1-cyano-2-methoxy-2-oxoethylidene)hydrazinyl)benzenesulfonate (NaHL₃) were used in the template synthesis of a series of CuII and CoII complexes [Cu(H₂O)₂L₁][H₂O] (1), [Cu(H₂O)(3-pyon)L₁][H₂O] (2), [Cu(H₂O)(4-pyon)L₁][H₂O] (3), [Co(H₂O)((CH₃)₂NCHO)(µ-L₂)₂][CH₃CN] (4), [Cu₃(µ₃-OH)(µ-OH)(µ₃-OH)(µ₂-X)(µ₂-HL₃)] (5), [Cu(H₂O)(py)L₁][H₂O] (6), [Cu(H₂O)(µ-L₁)]₆·6H₂O (7), [Cu(2-cnpyb)₂(L₁)₂]·2H₂O (8), [Cu(2-cnpyb)₂(L₁a)₂]·2H₂O (9), and [Cu(H₂O)(4-cnpy)(L₁a)] (10), where 3-pyon = 1-(pyridin-3-yl)ethanone, 4-pyon = 1-(pyridin-4-yl)ethanone, py = pyridine, HX = syn-2-pyrindinealdoxime, 4-cnpy = 4-cyanopyrdine; 2-cnpyb, 2-cnpyb, L₁a, L₁b, L₂a are the ligands derived from nucleophilic attack of methanol (a) or water (b) on a cyano group of 2-cyanopyridine (2-cnpy), L₁ or L₂, respectively, giving the corresponding iminoesters (2-cnpyb, L₁a or L₂a) or carboxamides (2-cnpyb or L₁b). An auxiliary ligand, namely syn-2-pyrindinealdoxime or pyridine, acting cooperatively with the metal ion (CuII in this case), induced an E/Z isomerization of the H₂L₄ ligand; the E- and Z-isomers were isolated separately and fully characterized (compounds 9 and 10, respectively). A one-pot activation of nitrile groups in different molecules was achieved in the syntheses of 8 and 9. Complexes 1–10 are catalyst precursors for the solvent-free microwave (MW) assisted selective oxidation of secondary alcohols to the corresponding ketones, with typical yields in the 29–99 % range (TOFs up to 4.94 x 10³ h⁻¹) after 30 min of MW irradiation.
A series of six new mixed-ligand dinuclear Mn(II,II) complexes of three different hydrazone Schiff bases (H₃L¹, H₃L², and H₃L³), derived from condensation of the aromatic acid hydrazides benzyldrazide, 2-aminobenzyldrazide, or 2-hydroxybenzyldrazide, with 2,3-dihydroxy benzaldehyde, respectively, is reported. Reactions of Mn(NO₃)₂·4H₂O with the H₃L¹⁻³ compounds, in presence of pyridine (1:1 mole ratio), in methanol at room temperature, yield [Mn(H₃L¹)(py)(H₂O)]₂(NO₃)₂·2H₂O (1·2H₂O), [Mn(H₃L²)(py)(CH₃OH)]₂(NO₃)₂·4H₂O (2·4H₂O) and [Mn(H₃L³)(py)(H₂O)]₂(NO₃)₂ (3) respectively, whereas the use of excess pyridine yields complexes with two axially coordinated pyridine molecules at each Mn(II) centre, viz. [Mn(H₃L¹)(py)₂]₂(NO₃)₂·H₂O (4·H₂O), [Mn(H₃L²)(py)₂](NO₃)₂·2H₂O (5·2H₂O) and [Mn(H₃L³)(py)₂](NO₃)₂·2CH₃OH (6·2CH₃OH), respectively. In all the complexes, the (H₃L¹⁻³⁻) ligand coordinates in the keto form. Complexes 1·2H₂O, 2·4H₂O, 4·H₂O, 5·2H₂O and 6·2CH₃OH are characterized by single crystal X-ray diffraction analysis. The complexes 1, 2 and 6, having different coordination environments, have been selected for variable temperature magnetic susceptibility measurements to examine the nature of magnetic interaction between magnetically coupled Mn(II) centres and also for exploration of the catalytic activity towards microwave assisted oxidation of alcohols. A yield of 81% (acetophenone) is obtained using a maximum of 0.4% molar ratio of catalyst relatively to the substrate in the presence of TEMPO and in aqueous basic solution, under mild conditions.

[CoCl(μ-Cl)(HpzPh)₃] (1) and [CoCl₂(HpzPh)₄] (2) were obtained by reaction of CoCl₂ with HCl(pzPh)₃ and HpzPh, respectively (HpzPh=3-phenylpyrazole). The compounds were isolated as air-stable solids and fully characterized by IR and far-IR spectroscopy, MS (ESI+/-), elemental analysis, cyclic voltammetry (CV), controlled potential electrolysis, and single-crystal X-ray diffraction. Electrochemical studies showed that 1 and 2 undergo single-electron irreversible Coᴵᴵ⁻Coᴵᴵᴵ oxidations and Coᴵ⁻Coᴵᴵ reductions at potentials measured by CV, which also allowed, in the case of
Oxido-renewable complexes bearing the water-soluble tris(pyrzol-1-yl)methanesulfonate, 1,3,5-triazas-7-phosphaadamantane, or related ligands, as catalysts for Baeyer-Villiger oxidation of ketones.


New rhenium(VII or III) complexes [ReO₃(PTA)₂][ReO₄] (1) (PTA = 1,3,5-triazas-7-phosphaadamantane), [ReO₃(mPTA)][ReO₄]I (2) (mPTA = N-methyl-1,3,5-triazas-7-phosphaadamantane cation), [ReO₃(HMT)][ReO₄] (3) (HMT = hexamethylenetetramine), [ReO₄(η²-Tpm)(PTA)][ReO₄] (4) (Tpm = hydrotris(pyrzol-1-yl)methane, HC(pz)₃, pz = pyrazolyl), [ReO₃(Hpz)(HMT)][ReO₄] (5) (Hpz = pyrazolyl), [ReO(Tpms)(HMT)] (6) (Tpms = tris(pyrzol-1-yl)methanesulfonate, O₂SC(pz)₃) and [ReCl₃(N₂C(O)Ph)(PTA)] (7) have been prepared from the Re(VII) oxide Re₂O₇ (1-6) or, in the case of 7, by ligand exchange from the benzoyldiazenido complex [ReCl₃{N₂C(O)Ph}(Hpz)(PPh₃)₂], and characterized by IR and NMR spectroscopies, elemental analysis and electrochemical properties. Theoretical calculations at the DFT level of theory indicated that the coordination of PTA to both Re(III) and Re(VII) centers by the P atom is preferable compared to the coordination by the N atom. This is interpreted in terms of the Re–PTA bond energy and hard-soft acid-base theory.

The oxo-rhenium complexes 1-6 act as selective catalysts for the Baeyer-Villiger oxidation of cyclic and linear ketones (e.g., 2-methylcyclohexanone, 2-methylcyclopentanone, cyclohexanone, cyclopentanone, cyclobutanone and 3,3-dimethyl-2-butanol or pinacolone) to the corresponding lactones or esters, in the presence of aqueous H₂O₂. The effects of a variety of factors are studied toward the optimization of the process.

PHENYL CARBOHYDRAZONE CONJUGATED 2-OXOINDOLINE AS A NEW SCAFFOLD THAT AUGMENTS THE DNA AND BSA BINDING AFFINITY AND CASPASE DEPENDENT ANTI-PROLIFERATIVE ACTIVITY OF 1,10-PHENANTHROLINE BASED COPPER(II) COMPLEX


A new type of copper(II) complex, [CuL(phen)$_2$(NO$_3$)$_2$] (CuIP), where L ((E)-N'-((2-oxoindolin-3-ylidene)benzohydrazide) is a N donor ligand and phen is the N, N-donor heterocyclic 1,10-phenanthroline, has been synthesized. The phenyl carbohydrazone conjugated isatin-based ligand L and CuIP were characterized by elemental analysis, infrared, UV–Vis, $^1$H and $^{13}$C NMR and ESI-mass spectral data, as well as single-crystal X-ray diffraction. The interaction of calf thymus DNA (CT DNA) with L and CuIP has been investigated by absorption, fluorescence and viscosity titration methods. The complex CuIP displays better binding affinity than the ligand L. The observed DNA binding constant ($K_b = 4.15(\pm0.18) \times 10^5$ M$^{-1}$) and binding site size ($s = 0.19$), viscosity data together with molecular docking studies of CuIP suggest groove binding and/or a partial intercalative mode of binding to CT DNA. In addition, CuIP shows good binding propensity to the bovine serum albumin (BSA) protein, giving a $K_{BSA}$ value of $1.25(\pm0.24) \times 10^6$ M$^{-1}$. In addition, the docking studies on DNA and human serum albumin (HSA) CuIP interactions are consistent with the consequence of binding experiments. The in vitro anti-proliferative study establishes the anticancer potency of the CuIP against the human cervical (HeLa) and breast (MCF7) cancer cells; noncancer breast epithelial (MCF10a) cells have also been investigated. CuIP shows better cytotoxicity and sensitivity towards cancer cells over noncancer ones than L under identical conditions, with the appearance of apoptotic bodies.

A DIFFERENTIALLY SELECTIVE CHEMOSENSOR WITH FLUORESCENCE OFF-ON RESPONSES ON CU$^{2+}$ AND ZN$^{2+}$ IONS IN AQUEOUS MEDIA AND APPLICATIONS IN PYROPHOSPHATE SENSING, LIVE CELL IMAGING AND CYTOTOXICITY


A new benzyol hydrazone based chemosensor R is synthesized by Schiff base condensation of 2,6-diformyl-4-methyl phenol and phenyl carbohydrazone and acts as a highly selective fluorescence sensor for Cu$^{2+}$ and Zn$^{2+}$ ions in aqueous medium. Reaction of R with CuCl$_2$ or ZnCl$_2$ forms the corresponding dimeric dicopper(II) [Cu$_2$(R)(CH$_3$O)(NO$_3$)$_2$]$_2$(CH$_3$O)$_2$ (R-Cu$^{2+}$) and dizinc(II) [Zn$_2$(R)$_2$(NO$_3$)$_2$] (R-Zn$^{2+}$) complexes which are characterized, as R, by conventional techniques including X-ray single
crystal analysis. Electronic absorption and fluorescence titration studies of R with different metal cations in CH\textsubscript{3}CN/0.02 M HEPES buffer medium (pH = 7.3) show a highly selective binding affinity only toward Cu\textsuperscript{2+} and Zn\textsuperscript{2+} ions even in the presence of other commonly coexisting ions such as Na\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Mn\textsuperscript{2+}, Fe\textsuperscript{3+}, Co\textsuperscript{3+}, Ni\textsuperscript{2+}, Cd\textsuperscript{2+} and Hg\textsuperscript{2+}. Quantification of the fluorescence titration analysis shows that this chemosensor R can indicate the presence of Cu\textsuperscript{2+} and Zn\textsuperscript{2+} even at very low concentrations of 17.3 and 16.5 ppb, respectively. R-Zn\textsuperscript{2+} acts as a selective metal based fluorescent sensor for inorganic pyrophosphate ion (PPi) even in the presence of other common anions such as F\textsuperscript{−}, Cl\textsuperscript{−}, Br\textsuperscript{−}, I\textsuperscript{−}, CH\textsubscript{3}COO\textsuperscript{−}, CO\textsubscript{3}\textsuperscript{2−}, HCO\textsubscript{3}−, N\textsubscript{3}−, SO\textsubscript{4}\textsuperscript{2−}, Pi, AMP, ADP, and ATP in aqueous medium. The propensity of R as a bio-imaging fluorescent probe to detect Cu\textsuperscript{2+} and Zn\textsuperscript{2+} ions in human cervical HeLa cancer cell lines and their cytotoxicity against human cervical (HeLa), breast (MCF7) cancer and noncancer breast epithelial (MCF10) cells have also been investigated. R-Cu\textsuperscript{2+} shows better cytotoxicity and sensitivity toward cancer cells over noncancer cells than R and R-Zn\textsuperscript{2+} under identical conditions, with the appearance of apoptotic bodies.


**RADICAL DECOMPOSITION OF HYDROGEN PEROXIDE CATALYZED BY AQUA COMPLEXES**

\[ [\text{M(H}_2\text{O)}\text{n}]^{2+} \quad (\text{M} = \text{Be}, \text{Zn}, \text{Cd}) \]

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The catalytic activity of the aqua complexes [M(H\textsubscript{2}O\textsubscript{n})\textsuperscript{2+}] (I) (M = Be, n = 4; M = Zn, Cd, n = 6) toward the radical decomposition of H\textsubscript{2}O\textsubscript{2} and generation of the HO\textsuperscript{•} radicals was investigated in detail by theoretical (DFT) methods. It was predicted and then confirmed by preliminary experiments that complexes I are able to catalyze this process despite the metals have only one stable non-zero oxidation state and, hence, cannot change it during the reaction as proposed in the classical Fenton chemistry. The mechanism of the H\textsubscript{2}O\textsubscript{2} decomposition includes the substitution of a water ligand for H\textsubscript{2}O\textsubscript{2}, protolysis of the coordinated H\textsubscript{2}O\textsubscript{2}, second H\textsubscript{2}O-for-H\textsubscript{2}O\textsubscript{2} substitution, elimination of one ligated water molecule (for Zn and Cd), and the homolytic HO–OH bond cleavage in complexes [M(H\textsubscript{2}O\textsubscript{n})(H\textsubscript{2}O\textsubscript{2})(OOH)]\textsuperscript{•}. The principal factors affecting the HO\textsuperscript{•} formation are lability of the complexes, their acidity, and their ability to activate H\textsubscript{2}O\textsubscript{2} toward the homolytic HO–OH bond cleavage. The participation of two H\textsubscript{2}O\textsubscript{2} molecules is necessary for an efficient HO\textsuperscript{•} generation. The water substitution steps occur via concerted I\textsubscript{s} (Be, Cd) or dissociative D (Zn, Cd) mechanisms.
**Bio-Oils Upgrading for Second Generation Biofuels**

Inês Graça, José M. Lopes, Henrique S. Cerqueira, and Maria F. Ribeiro

The processing of biomass derived feedstocks (bio-oils) in existing refineries is a topic that has been receiving a lot of attention from both industry and academia in the last years. Lignocellulosic biomass feedstocks are complex mixtures of many oxygenated hydrocarbons. Its upgrading towards liquid fuels must include the oxygen removal, two main routes having been proposed: catalytic hydrodeoxygenation (HDO) and catalytic cracking. HDO has been performed at high hydrogen pressure, using catalysts based on those typically applied in conventional hydrotreating (HDT), as well as a new type of supported noble and transition metal catalysts. Catalytic cracking occurs at atmospheric pressure, using acid catalysts, mainly the active phases of fluid catalytic cracking catalysts (HY and HZSM-5 zeolites). The present review focuses on the upgrading possibilities of renewable non-edible feedstocks, obtained from biomass fast pyrolysis or liquefaction, in the petroleum refinery, towards the production of second generation biofuels. Special attention is devoted to the recent studies concerning the alternative of bio-oils co-processing together with crude oil feedstocks. In fact, although all these feedstocks have potential to be directly converted into transportation fuels in dedicated units, it seems more attractive to upgrade them in combination with conventional feedstocks.

**CO₂ Hydrogenation into CH₄ on NiHNaUSY Zeolites**

I. Graca, I, LV Gonzalez, MC Bacariza, A. Fernandes, C. Henriques, JM Lopes, MF Ribeiro

CO₂ hydrogenation into methane was carried out over catalysts containing nickel and cerium species supported on a HNaUSY zeolite, using an H₂/CO₂ ratio of 4 and temperatures ranging from 250 to 450 °C. Significant CO₂ conversion and CH₄ selectivity were achieved for Ni-zeolite catalysts prepared by impregnation. Conversion increased with the Ni content from 2 to 14%, due to the higher amount of Ni species after reduction. A further enhancement of the catalysts performances was noticed when doping the Ni-zeolites catalysts with 3-15% of Ce. Actually, the presence of CeO2 after reduction might promote CO2 activation into CO, the final catalyst properties being due to the synergetic effect between the metal active sites and the promoter. Furthermore, almost no deactivation due to sintering was observed after 10 h of reaction at 400 °C. Comparing these results with those reported in literature it is possible to conclude that zeolites
have great potential to be used as catalyst supports for the CO$_2$ methanation reaction. In fact, taking the commercially available and widely used HNaUSY zeolite, it was possible to reach conversion and selectivity similar to those previously found in the literature for the best CO$_2$ methanation catalysts that use potentially more expensive bulk cerium oxide supports, even without performing any optimization of the zeolite support.

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**INVESTIGATION OF THE NATURE OF SILVER SPECIES ON DIFFERENT AG-CONTAINING NOX REDUCTION CATALYSTS: ON THE EFFECT OF THE SUPPORT**

R. Bartolomeu, B. Azambre, A. Westermann, A. Fernandes, R. Bértolo, C. Henriques, P. Da Costa, Filipa Ribeiro

Ag/zeolite catalysts have been reported to achieve interesting conversions using propane or ethanol as reducing agent for NOx selective catalytic reduction (SCR)$^{1,2}$. This work contains a detailed study on silver species present in four different Ag-based catalysts, with different supports (Al$_2$O$_3$, ceria-zirconia, sulphated ceria-zirconia and MFI zeolite), which were identified by a combination of different characterization techniques. Each support stabilizes specific Ag species with different activity for NOx SCR. The activity of these different catalysts on NOx SCR with ethanol was evaluated and a possible redox cycle between Ag$_2$O/Ag$^0$ or Ag$^+/Ag$$_{n}$$^{2+}$ was proposed.

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**OPTIMAL DESIGN OF REACTIVE DISTILLATION SYSTEMS: APPLICATION TO THE PRODUCTION OF ETHYL TERT-BUTYL ETHER (ETBE)**

Luís Domingues, Carla I.C. Pinheiro, Nuno M.C. Oliveira

This work addresses the design of reactive distillation columns to produce ETBE, based on a detailed first-principles model that considers equilibrium and kinetic information, rigorous physical property data, and catalyst deactivation. An evolutionary algorithm is used to generate a sequence of feasible designs with improved characteristics in a sequential solution/optimisation strategy, by specifying the design variables (both integer and continuous) that characterise a particular column configuration. Two classes of optimisation algorithms are compared: genetic algorithms and particle swarm optimisation. The objective function considered is the gross annual profit. The results demonstrate that both algorithms are adequate to solve this design problem. The effect of catalyst deactivation included in the design stage played a determinant role in the optimal column specification. A post-design sensitivity analysis is developed to assess the quality of the solutions obtained, together with the individual effects of each design variable in the optimal configuration identified.
Many synthesis strategies can be used to improve the physicochemical properties of heterogeneous catalysts like zeolites and silicoaluminophosphates. However, the increasing demand of faster diffusion rates and conversion of bulkier molecules makes the relatively limited size of channels in zeolites and SAPOs to become a severe drawback when used as solid acid catalysts in hydrocarbons transformations. One interesting strategy to overcome such diffusion limitations consists in preparing hierarchical porous materials, i.e. catalysts with complementary micro and mesoporous systems that allow reactants to reach quickly the catalytic active sites and products to desorb easily. In the present study, the chemical surface of carbon matrixes used as secondary mesopores templating agents was shown to have an important effect on the nature of the different species involved in the initial gels and on the physicochemical and catalytic properties of the final silicoaluminophosphate (SAPO-11) materials. Although these solid templates have been reported in the literature to be inert materials, this preliminary study shows that the modification of the surface chemistry of the carbons seems to promote interactions with the synthesis gel, resulting in the production of SAPO-11 materials with different acid properties and enhanced catalytic behavior.
supported catalytic systems is affected by changes in either the surface chemistry or the textural properties of the support, and the relative contribution of these factors determines the final activity. For metallocene catalysts supported on micro- or nanosized MCM-41 surfaces, it turns out that differences in catalytic activity are more dependent on the preceding surface silanol distribution than on particle size and diffusion constraints. This silanol distribution is altered by silane functionalization and a beneficial or detrimental influence may be observed as a function of the initial state. The dispersion of MCM-41 within the PE matrix is also dependent on particle size and its functionalization. Accordingly, the decrease in particle size favors particle-polymer interactions allowing a better particle distribution and the polymerization from support/filler surface seems to hinder agglomeration. Therefore, MCM-41/high-density polyethylene (HDPE) hybrid materials with improved mechanical performance have been prepared by in situ polymerization using different silanes for the functionalization of either micro or nanosized mesoporous MCM-41 particles.


TUNABLE FLUOROPHORES BASED ON 2-(ARYLIMINO)PYRROLYL CHELATES OF DIPHENYLBORON: SYNTHESIS, STRUCTURE, PHOTOPHYSICAL CHARACTERIZATION AND APPLICATION IN OLEDs

D. Suresh, Patrícia S. Lopes, Bruno Ferreira, Cláudia A. Figueira, Clara S. B. Gomes, Pedro T. Gomes, Roberto E. Di Paolo, António L. Maçanita, M. Teresa Duarte, Ana Charas, Jorge Morgado, Maria José Calhorda

Light emitting molecules play important roles as sensors, in solar energy conversion, in optoelectronic devices. Several aspects of the synthesis, molecular structure, and photophysical characterization of a new family of highly photoluminescent tetracoordinate boron complexes are being investigated. These organoboron derivatives contain a bidentate 2-iminopyrrolyl ligand that can be fine-tuned either electronically or sterically, leading to different emission colours. Diverse strategies used for the tuning of these compounds are being employed. These complexes are good emitters in electroluminescent layers of Organic Light Emitting Diode (OLED) devices.
Radical reactions of titanium(III) complexes 1 and 2 are described. Reactions with neutral electron acceptors led to metal oxidation to Ti(IV), 4 being formed with the TEMPO radical and 9 with PhN=NP. The latter complex was also formed when 1 was oxidized by [Cp₂Fe][BPh₄], but the [Cp₂Fe][PF₆] analogue yielded 8. The reactions of 1 or 2 with O₂ gave [Ti(tBu₂O₂NN')Cl₂(µ-O)], 3. The reaction is exergonic (ΔG = -123.6 kcal∙mol⁻¹), according to DFT calculations. [Ti(tBu₂O₂NN')(CH₂Ph)(S)] (S = THF, 5; py, 6) are not stable in solution and gave 1:1 co-crystals of [Ti(tBu₂O₂NN')(CH₂Ph)₂], 7 and 3, most probably resulting from a disproportionation process of titanium(III) followed by oxygen abstraction by the resulting Ti(II) species.

The oxidation of [Ti(tBu₂O₂NN')(κ²-{CH₂-2-(NMMe₂)-C₆H₄})] led to a complex mixture. Recrystallization of this mixture led to a 1:1 co-crystal of two coordination isomers of the titanium oxo dimer 3. In one of these isomers, one metal is pentacoordinate and the dimethylamine moiety of the diamine bis(phenolate) ligand is not bonded to the metal, displaying a coordination mode of the ligand never observed before. The other titanium centre is distorted octahedral with two cis-phenolate moieties. In the second isomer, the coordination of the two ancillary ligands to the titanium centres reveals mutually cis-phenolate groups in one half of the molecule and trans-coordinated in the other titanium centre, keeping a distorted octahedral environment around each titanium.

This is the first systematic study on the reactivity of paramagnetic titanium(III) complexes of a non-metalloocene system. The results revealed that these species are very reactive, presenting several reaction patterns that are extremely sensitive to the experimental conditions. Cationic complexes of Ti(IV) tend to balance its extreme acidity by abstracting X type ligands or oxygen from the medium. Along with these rearrangements the ancillary ligand may display hemilabile behaviour. Although not identified in the many processes mediated by titanium diamine bis(phenolate) complexes described to date, the results reported here are relevant for the outlining of the applications of these compounds.
Synthesis and Catalysis


**DIAZOO- AND TRANSITION METAL-FREE C-H INSERTION: A DIRECT SYNTHESIS OF B-LACTAMS**

Luis F. R. Gomes, Luis F. Veiros, Nuno Maulide, Carlos A. M. Afonso

β-lactams are important building blocks in organic synthesis normally obtained by cycloadditions and C–H insertion reactions on carbone species resulting from metal catalysed decomposition of diazo-precursors. A novel process for the synthesis of β-lactams was developed, in which the lactams are formed in a single step from β-ketoamines via iodonium ylides. This is a diazo-metal and metal-free process and occurs under very mild conditions. DFT studies proved that the reaction mechanism involves a free carbone intermediate.

**NANOSTRUCTURED SILICA MATERIALS IN OLEFIN POLYMERISATION: FROM CATALYTIC BEHAVIOUR TO POLYMER CHARACTERISTICS**

João M. Campos, João Paulo Lourenço, Henri Cramail, M. Rosário Ribeiro

This paper reviews progress in organometallic α-olefin polymerisation catalysts supported on zeolites or mesoporous silicas, discussing the role of these nanostructured materials in establishing new catalytic behaviours and polymer properties. Zeolites and other nanostructured materials show unique structural and surface features that have been used with advantage in the immobilisation of a large variety of catalysts, including α-olefin polymerisation catalysts such as metallocene complexes. The characteristics of these materials, such as the ordered porous system, the large surface area and a tuneable acidity have a great impact on the immobilisation of the catalyst, with implication on the formation and nature of active species and polymerisation activity. Methods of preparation, diffusion limitations and confinement effects are rationalised and their role on the catalytic system and final polymer properties is discussed. This review is mainly focused on metallocene catalysts but examples of post-metallocene catalysts and olefin polymerisation behaviour of non-organometallic complexes, covering Ziegler-Natta Ti/V catalysts and Phillips Cr catalysts, as well as metal-modified mesoporous carriers are described and discussed. Additionally, the effects of the nanostructured supports on the morphologies and physical properties of the polyolefins are also covered, and an account is made on how mesoporous materials can be used in the preparation of novel polyolefin nanoblends and nanocomposites.
NEW OXOVANADIUM(IV) N-ACYLHYDRAZONE COMPLEXES: PROMISING ANTILEISHMANIAL AND ANTITRYPANOSOMAL AGENTS


Searching for new promising metal-based hits against Trypanosoma cruzi and Leishmania parasites, two related VIVO N-acylhydrazone complexes, [VIVO(LASSBio1064-2H)(H2O)], I, and [VIVO(LASSBio1064-2H)(phen)]·(H2O), 2, where LASSBio1064 is (E)-N0-(2-hydroxybenzylidene-4-chlorobenzohydrazide and phen is 1,10-phenanthroline, were synthesized, and characterized and evaluated on T. cruzi and Leishmania major. Their unspecific cytotoxicity was tested against murine macrophages. To provide insight into mechanism of its antiparasitic action, 2 its DNA interaction ability was evaluated on plasmid DNA by atomic force microscopy (AFM), and on CT DNA by using DNA viscosity measurements and fluorescence spectroscopy. The complexes, and particularly 2 were active in vitro against the epimastigote form of T. cruzi (Tulahuen 2 strain) showing IC₅₀ values significantly lower than that of the reference trypanosomicidal drug Nifurtimox. The compounds show low toxicity on mammalian cells (IC₅₀ > 100 mM). DNA interaction studies pointed out at DNA as a potential target in the parasite. The results suggest that [VIVO(LASSBio1064-2H)(phen)].(H2O) may be a promising compound for further drug development stages.

INTERACTION OF VANADIUM(IV) WITH HUMAN SERUM APO-TRANSFERRIN


Transport proteins such as transferrin (hTF) are likely to play key roles in the transport of therapeutic vanadium compounds to tissues. However, only the closed form of hTF is recognized by transferrin cell receptors.

In this work the interaction of VIVO-salts as well as of a few VIVO(carrier)n complexes with hTF is addressed focusing on the determination of the nature and stoichiometry of the binding of VIVO²⁺ to hTF, and whether the VIVO-hTF species formed are recognized or not by transferrin cell receptors. For VIVO salts and several VIVO(carrier)ₙ complexes (carrier = maltolato, deferiprone, picolinato and dipicolinato) the maximum number of VIVO²⁺ bound per hTF is ~2 or lower in all cases. As concluded by urea gel electrophoresis experiments, the formation of (VIVO)₂hTF species occurs with the closing of the hTF conformation, as is the case in (Fe³⁺)₂hTF. Thus, this essential feature for the transferrin receptor recognition is fulfilled by (VIVO)₂hTF.
SCREENING ORGANOMETALLIC BINUCLEAR THIOSEMICARBAZONE RUTHENIUM COMPLEXES AS POTENTIAL ANTI-TUMOUR AGENTS: CYTOTOXIC ACTIVITY AND HUMAN SERUM ALBUMIN BINDING MECHANISM


Ruthenium complexes are recognized as an effective alternative to Pt-based agents for the treatment of cancer, affording different mechanisms of action, a different spectrum of activity and the potential to overcome Pt-resistance, as well as a general lower toxicity.

Four complexes combining the \{Ru(p-cym)\} moiety (p-cym = para-cymene) with thiosemicarbazone ligands containing the 5-nitrofuryl pharmacophore were investigated in vitro. The compounds are dimeric structures of general formula \[\text{[Ru}_2(p\text{-cym})_2(L)_2\text{-X}_2]\] where \(X = \text{Cl}^-, \text{PF}_6^-\) and \(L = \) deprotonated 5-nitrofuraldehyde TSC (L1), and the N-methyl (L2), N-ethyl (L3) and N-phenyl (L4) derivatives.

Compounds 1-4 were screened in vitro for their cytotoxicity against a range of human cancer cell lines (HL-60 acute promyelocytic leukemia, A2780 ovarian adenocarcinoma, MCF7 breast adenocarcinoma and PC3 grade IV prostate carcinoma).

VANADIUM COMPLEXES AS PROSPECTIVE THERAPEUTICS: STRUCTURAL CHARACTERIZATION OF A V(IV) LYSOZYME ADDUCT


The biological activity of vanadium complexes, namely, as insulin enhancers, is well known, and interaction with proteins is relevant in this respect. We report a combined X-ray crystallography, EPR and DFT study of the interaction of vanadium picolinate complexes with hen egg white lysozyme (HEWL). We show that the \(\text{V}^{\text{IV}}\text{O(pic)}_2\) complex covalently binds to the \text{COO}^-\text{group of the side chain of Asp52 of HEWL. The long V}^{\text{IV}}=\text{O bond obtained in the X-ray study is explained as due to reduction of V}^{\text{IV}}\text{ to V}^{\text{III}}\text{ during exposure of the crystals to the intense X-ray beam. This is the first ever reported x-ray diffraction of a V}^{\text{IV}}\text{O-compound with a protein.}
HYDROXYQUINOLINE DERIVED VANADIUM (IV AND V) AND COPPER (II) COMPLEXES AS POTENTIAL ANTI-TUBERCULOSIS AND ANTI-TUMOR AGENTS

Tuberculosis is a pulmonary infection disease initiated by the pathogenic bacteria *Mycobacterium tuberculosis* (Mtb) and it is still a leading cause of human mortality in the world. Therefore new alternative compounds for the treatment of tuberculosis are required. Several mixed ligand vanadium and copper complexes containing 8-hydroxyquinoline (8HQ) were prepared and the biological activity of the compounds assessed against Mtb and the cytotoxic activity and selectivity evaluated. Almost all tested vanadium complexes were very active against Mtb and the MICs were comparable to, or better than, the MICs of drugs, such as streptomycin. The complexes were also significantly more active than cisplatin. However, for most of them the selectivity toward cancer cells was poor.

NEW TRIS-3,4-HOPO LANTHANIDE COMPLEXES AS A POTENTIAL IMAGING PROBES. COMPLEX STABILITY AND MAGNETIC PROPERTIES

This article examines the properties of a new class of lanthanide complexes with a tripodal tris-3-hydroxy-4-pyridinone (Tris-3,4-HOPO) ligand NTP(PrHP)₃ as potential diagnostic probes. This hexadentate ligand enables the formation of 1:1 Ln³⁺ complexes (Ln = La, Pr, Gd, Er, Lu) with high thermodynamic stability, while the magnetic properties of Gd-chelates show improved relaxivity (higher hydration number), as compared with commercially available Gd-based contrast agents (CAs). Therefore, NTP(PrHP)₃ emerges as part of a new generation of ligands for CAs with imaging sensibility gains.
SEARCHING FOR NEW ALUMINIUM CHELATING AGENTS: A FAMILY OF HYDROXYPYRONE LIGANDS

A series of new tetradeutate Al-chelators with two kojic units joined by different linkers has been developed and evaluated in solution in vivo. Huge advantages of these molecules are that they are easy and cheap to produce. The high stability of Al$^{3+}$ complexes and the biodistribution profile gave evidence of the ability to scavenge Al/Fe from the body. The complexation studies involved potentiometry, ESI-MS, $^1$H NMR, X-ray diffraction and QM calculations. The in vivo studies show that these bis-kojic derivatives induce faster clearance from main organs than the monomeric analogue.

FIRST POLYMER “RUTHENIUM-CYCLOPENTADIENYL” COMPLEX AS POTENTIAL ANTICANCER AGENT
A. Valente, M.H. Garcia, F. Marques, Y. Miao, C. Rousseau, P. Zinck

Our recent work in the frame of macromolecular metallodrugs led to the identification of the first Ru(II)-cyclopentadienyl’ polymer-conjugate (RuPMC), [CpRu(PPh$_3$)(L)]$^+$ (L = D-glucose end-capped polylactide macroligand). This compound is cytotoxic against human MCF7 and MDAMD231 breast and A2780 ovarian adenocarcinoma with IC$_{50}$ values in the µM range. ICP-MS studies showed that the Ru-polymer conjugate enters the MCF7 ER$^+$ cancer cells and is retained ca. 50% in the nucleus demonstrating its application as a therapeutic agent in, for example, hormone-responsive cancers. Our ruthenium-polymer complexes incorporate several features to overcome many of the current limitations of the conventional chemotherapy approaches: i) a tumour-specific molecule attached to the polymeric chain; ii) high molecular weight polymers that will be specific to solid tumours by the known EPR effect; and iii) a cytotoxic fragment based on the “RuCp” core. Our approach differs from those already reported, and we expect that it will lead to different reactivity patterns and thus a distinct model of behaviour.
Anticancer activity of the new [Ru(η⁵-C₅H₅)(PPh₃)(Me₂bpy)][CF₃SO₃] was evaluated \textit{in vitro} against several human cancer cell lines. Remarkably, the IC₅₀ values, placed in the nM to \(\mu\)M range, largely exceeded the activity of cisplatin. Binding to HSA does not affect the complex activity. The studies of interactions with HSA done by fluorescence spectroscopy revealed that the present Ru-complex strongly quenches the intrinsic fluorescence of albumin. Cell death by [Ru(η⁵-C₅H₅)(PPh₃)(Me₂bpy)][CF₃SO₃] was reduced in the presence of endocytosis' modulators and at low temperature, suggesting an energy-dependent mechanism consistent with endocytosis.

A novel water soluble organometallic compound, [RuCp(mTPPMSNa)(bipy)][CF₃SO₃] (TM85, \(\text{Cp}=\eta^5\)-mTPPMS = diphenylphosphane-benzene-3-sulfonate) was synthesized. Studies of interactions with relevant proteins were done by electrochemical and fluorescence, showing that TM85 strongly binds to HSA. Studies carried out to study the formation of TM85 adducts with ubiquitin and cytochrome c were done by ESI-MS. This compound is cytotoxic against a variety of human cancer cell lines, but this effect was reduced in the presence of endocytosis modulators at low temperatures, suggesting an energy-dependent mechanism consistent with endocytosis. Ultrastructural analysis by TEM revealed that TM85 targets the endomembranar system disrupting the Golgi and also affects the mitochondria. Disruption of plasma membrane observed by flow cytometry could lead to cellular damage and cell death.
IMPORTANT CYTOTOXICITY OF NOVEL IRON(II) CYCLOPENTADIENYL COMPLEXES WITH IMIDAZOLE BASED LIGANDS
A. Valente, A. M. Santos, L. Côrte-Real, M. Paula Robalo, Y. Moreno, M. Font-Bardia, T. Calvet, J. Lorenzo, M. H. Garcia

Two new families of “Fe\(^{II}\)(η\(^5\)-C\(_5\)H\(_5\))” half sandwich compounds bearing a N-heteroaromatic ligand were obtained. All compounds revealed excellent cytotoxic properties against several human cancer cell lines. These are the first studies concerning the evaluation of “Fe\(^{II}\)(η\(^5\)-C\(_5\)H\(_5\))” half sandwich complexes as anticancer agents. Considering that Fe is a very abundant, cheap and a biologically essential transition metal, this new family of Fe compounds can certainly be a breakthrough in the cancer chemotherapy frame.

THE PHENOLIC METABOLITES OF THE ANTI-HIV DRUG EFAVIRENZ: EVIDENCE FOR DISTINCT REACTIVITIES UPON OXIDATION WITH FRÉMY’S SALT.
Shrika H. Harjivan, Riccardo Wanke, Joaão L. Ferreira da Silva, M. Matilde Marques, Alexandra M. M. Antunes

Efavirenz (EFV) is a non-nucleoside reverse transcriptase inhibitor administered as first line treatment against HIV-1. The major drawbacks of EFV therapy are neurotoxicity and hepatotoxicity, which may result from bioactivation to reactive metabolites capable of reacting with bionucleophiles. We investigated the in vitro oxidation of the phenolic EFV metabolites, 7-OH-efavirenz and 8-OH-efavirenz (8-OH-EFV), with Frémy’s salt. 8-OH-efavirenz was demonstrated to be more prone to oxidative degradation than 7-OH-efavirenz, yielding multiple oxidation products stemming from a quinone-imine intermediate. In contrast, a quinoline derivative was selectively obtained from 7-OH-EFV. These observations demonstrate a remarkable difference in the reactivities of the two phenolic EFV metabolites under oxidative conditions. Moreover, taking into consideration the toxicological significance of quinone–imine derivatives, these findings may explain earlier reports that 8-OH-efavirenz is a more potent toxicant than 7-OH-efavirenz in model test systems.

MONITORTING ABACAVIR BIOACTIVATION IN HUMANS: SCREENING FOR AN ALDEHYDE METABOLITE

Nádia M. Grilo, Alexandra M. M. Antunes, Umbelina Caixas, Aline T. Marinho, Catarina Charneira, M. Conceição Oliveira,b M. Matilde Marques, Sofia A. Pereira

The anti-HIV drug abacavir (ABC) is associated with idiosyncratic hypersensitivity reactions and cardiotoxicity. This work represents the first evidence of ABC bioactivation in humans upon identification of a ABC adduct formed with N-terminal valine of hemoglobin isolated from HIV patients. This data confirms the ability of ABC to modify self-proteins and suggest that the molecular mechanism(s) of some ABC-induced adverse reactions may require bioactivation. Therefore, the results reported herein demonstrate that the search for causal relationships between the formation of ABC-derived protein adducts and the occurrence of ABC-induced toxic events in human patients is worth pursuing. Moreover, the adduct characterization methodology described in the present study is simple, sensitive, accurate, reliable, and applicable to high throughput analyses, as required for testing clinical samples. As such, it is of significant worth for further toxicological studies.


THE ROLE OF COMPETITIVE BINDING TO HUMAN SERUM ALBUMIN ON EFAVIRENZ-WARFARIN INTERACTION: A NUCLEAR MAGNETIC RESONANCE STUDY

Shrika H. Harjivan, Riccardo Wanke, Sofia A. Pereira, M. Matilde Marques, Alexandra M. M. Antunes

The potential for co-prescription of the anti-human immunodeficiency virus (anti-HIV) drug efavirenz (EFV) and the oral anticoagulant warfarin (WAR) is currently high as EFV is a drug of choice for HIV type 1 infection and because cardiovascular disease is increasing among HIV-infected individuals. However, clinical reports of EFV–WAR interaction, leading to WAR overdosing, call for elucidation of the mechanisms involved in this drug–drug interaction. Here we present the first report demonstrating competition of the two drugs for the same binding site of human serum albumin. Using ligand-based nuclear magnetic resonance experiments, this study proves that EFV has an effect on the concentration of free WAR. This previously unidentified EFV–WAR interaction represents a potential risk factor that should be taken into account when considering treatment options.
The slow molecular mobility in the active pharmaceutical ingredient probucol was studied by Thermally Stimulated Depolarisation Currents (TSDC) in the temperature region between -130 ºC and 50 ºC. The distribution of relaxation times was characterized for the secondary relaxations and for the glass transition relaxation. Based on aging results we were able to draw distinctions between the fast secondary relaxations on the one hand, and the slow-beta or Johari-Goldstein relaxation on the other.

The steepness index of probucol was calculated from the temperature dependent relaxation time of the glass transition and using methods based on the influence of the scanning rate on the glass transition signal (in DSC and TSDC). The obtained values show some scattering but they are in the frontier between the fragile and strong behaviors.

The study of structure–energetics relationships for active pharmaceutical ingredients has received considerable attention in recent years, due to its importance for the effective production and safe use of drugs. In the present work the widely prescribed cholesterol-lowering drug simvastatin was investigated by combining experimental (combustion calorimetry and differential scanning calorimetry) and computational chemistry (quantum chemistry and molecular dynamics calculations) results. The studies addressed the crystalline form stable at ambient temperature (form I) and the liquid and gaseous phases. Heat capacity determinations by DSC showed no evidence of polymorphism between 293 K and the fusion temperature [1]. It was also found that the most stable molecular conformation in the gas phase given by the quantum chemistry calculations (B3LYP-D3/cc-pVTZ) is analogous to that observed in the crystal phase. The molecular dynamics simulations correctly captured the main structural properties of the crystalline phase known from published single crystal X-ray diffraction results (unit cell dimensions and volume). They also suggested that, while preferential conformations are exhibited by the molecule in the solid at 298.15 K, these preferences are essentially blurred upon melting.
GABAPENTIN COORDINATION NETWORKS: MECHANOCHEMICAL SYNTHESIS AND BEHAVIOUR UNDER SHELF CONDITIONS
Sílvia Quaresma, Vânia André, Alexandra Antunes, Luís Cunha-Silva, M. Teresa Duarte

Active pharmaceutical ingredients (API) coordination complexes and networks present a promising pathway for developing new bioinspired materials. In the present study, we report several coordination networks of gabapentin with Y(III), Mn(II), and several lanthanides (LnCl₃), Ln = La³⁺, Ce³⁺, Nd³⁺, Er³⁺ obtained by mechanosynthesis. To the best of our knowledge, these are among the first coordination networks of pharmaceuticals involving lanthanides. These novel compounds proved to be unstable under shelf conditions, are thermally stable until water release at approximately 80 °C, and decompose above 200–250 °C. The coordination networks obtained present different structural architectures based on mono-, di-, tri-, and hexa-metallic centers (herein called monomers, dimers, trimers, and hexamers), and also a one-dimensional polymeric chain was obtained. Gabapentin chelation modes are the same in most of the networks, adopting three typical geometries: the bidentate coordination – chelation, mode I; the bridge coordination, mode II, and the “bidentate-bridge” coordination, mode III. NMR studies show that the compounds have different behavior in solution, where a single coordination mode seems to be present.

AN INSIGHT INTO DAPSONE CO-CRYSTALS: SULFONES AS PARTICIPANTS IN SUPRAMOLECULAR INTERACTIONS
Inês Martins, Marta Martins, Auguste Fernandes, Vânia André, M. Teresa Duarte

Herein we disclose a new pathway for the design of dapsone co-crystals exploring the formation of N–H⋅⋅⋅O/N interactions using amide and pyridinic derivatives as potential co-formers. Two new co-crystals of dapsone, a sulfonamide antibiotic, with ε-caprolactam and 4,4′-bipyridine have been synthesized preferentially by traditional solution techniques, but mechanochemistry has also been addressed. The full structural characterization of these forms is discussed and shows that: (a) in the co-crystal with ε-caprolactam the typical N-NH₂–O-SO₂ interactions of dapsone molecules and the cages formed between them are disrupted by a new N-NH₂–O-CONH interaction, in which ε-caprolactam molecules further form amide–amide R₂(8) synths and (b) in the co-crystal with 4,4′-bipyridine, the N-NH₂–O-SO₂ interactions between dapsone molecules are maintained and additional N-NH₂–N-pyridine interactions are responsible for the formation of 4,4′-bipyridine channels between dapsone cages. Moreover, the thermal stability of these co-crystals is also discussed, showing that the co-formers leave the structure and hence the reported melting corresponds to the melting of pure dapsone.
TOWARDS THE RATIONAL BIOSYNTHESIS OF SUBSTITUTED PHENAZINES AND PHENOXAZINES BY LACCASES
Ana Catarina Sousa, M. Conceição Oliveira, Lígia O. Martins* and M. Paula Robalo*

Laccases are multi-copper oxidases that oxidise a wide range of substrates including phenol and aniline derivatives, which could be further involved in coupling reactions leading to the formation of dimeric and trimeric structures. The paper describes the enzyme-mediated dimerisation of several ortho and meta, para-disubstituted aromatic amines into phenazine (“head-to-tail” dimers) and phenoxazinone chromophores. The structure of novel enzymatically synthesised phenazine and phenoxazinone dyes using CotA laccase was assessed by NMR and MS. Overall our data show that this enzymatic green process is an efficient alternative to the classic chemical oxidation of aromatic amines and phenols, with an impact on the broad field of applications of these heterocyclic compounds.

EVALUATION OF THE PERFORMANCE OF THE DETERMINATION OF ANIONS IN THE WATER SOLUBLE FRACTION OF ATMOSPHERIC AEROSOLS
Arias A, Silva RJNB, Camões MFGFC, Oliveira CMRR

The knowledge of the mass of particulate matter in air, its chemical composition and emission sources is of relevance for taking decisions concerning air quality management in urban areas. The interpretation of these data is a function of the quality of the measurement results expressed by their uncertainties.

This study aimed at developing models of the performance of the determination of anions in the water-soluble fraction of atmospheric aerosols, capable of determining, separately, the contribution of aerosols sampling, extraction of water-soluble fraction of atmospheric aerosols and quantification, by ion chromatography, of anions in the extract. The sampling procedure was assessed from the dispersion of results of duplicate parallel sampling after subtracting the analytical component of this dispersion. These models are used to evaluate the adequacy of the measurement procedure for the determination of urban aerosol composition and to support strategies for reducing measurement uncertainty or cost of analysis.
BIOAVAILABILITY OF CADMIUM AND BIOCHEMICAL RESPONSES ON THE FRESHWATER BIVALVE CORBICULA FLUMINEA – THE ROLE OF TiO2 NANOPARTICLES
Gonçalo Vale, Cristiana Franco, Mário S. Diniz, Margarida M.C. dos Santos, Rute F. Domingos

The increasing and widespread applications of TiO2 engineered nanoparticles (nTiO2) led to the release of these materials into aquatic environments and consequently a change on the assessment of the environmental risk of trace metals. In this work the role of two commercially available nTiO2 with contrasting sizes and crystalline phases on Cd speciation, biouptake and toxicity for the freshwater bivalve Corbicula fluminea was investigated. Results showed that despite the decrease of free Cd concentration in freshwater due to the formation of Cd-nTiO2 surface complexes, Cd uptake by C. fluminea was similar in the absence and presence of the NPs. Additionally, several toxicological endpoints either triggered by Cd or the nTiO2 or Cd+nTiO2 were also observed: (i) significant increase in Catalase activity in presence of Cd+nTiO2, (ii) slight increase on the Lipid peroxidation in presence of the nTiO2 and (iii) morphological changes in the bivalve’s digestive gland for all treatments. To the best of our knowledge this is the first study on the biochemical responses of a freshwater bivalve to Cd in presence of nTiO2.

PATHWAYS AND SPECIATION OF MERCURY IN THE ENVIRONMENTAL COMPARTMENTS OF DECEPTION ISLAND, ANTARCTICA
André Mão de Ferro, Ana Mota, João Canário

Environmental studies in Deception Island are scarce, and are of great interest since it has potential sources of trace element related to the volcanic activity. This work was the first integrated mercury study in an Antarctic ecosystem. The aim of this study was to investigate the sources, transport and speciation of Hg regarding one of its most important methylated form, MeHg. The results obtained suggest that volcanic activity is the most important Hg source. Mercury levels in water and sediments sampled at two fumaroles were up to 10,000 times higher than in the other sampling sites. However, dissolved methylmercury (MeHg) was below the
detection limit in those samples, probably due to the very high temperature found in fumaroles (above 90 °C) inhibiting Hg biomethylation. Sediments collected at the same fumaroles showed a similar pattern: high levels of Hg (up to 10 mg Kg⁻¹) and no detected MeHg. Methylmercury proportion was surprisingly high in saline waters of Port Foster (13–33%), which suggested exceptional conditions for Hg methylation and low demethylation processes in the water column of Port Foster. A combination of factors such as the presence of important volcanic sources of Hg, lower light, temperature and anoxia gradient from top to bottom waters associated with high residence time of saline waters of Port Foster might have led to a higher concentration of Hg in those waters during winter which, in turn, will be available for methylation processes during the warmer months. Additionally, the high residence time of water in the Bay may also contribute to create an inner pool of volcanic mercury and MeHg available for aquatic organisms.
AGREGATION/DISAGGREGATION OF CHLOROPHYLL A IN MODEL PHOSPHOLIPID-DETERGENT VESICLES AND MICELLES
Raquel F. Correia, M. Isabel Viseu and Suzana M. Andrade

The photosynthetic pigments of higher plants exist in complex oligomeric states, which are difficult to study in vivo. To investigate aggregation processes of chlorophyll a (Chl a), we used an in vitro reconstitution procedure, with this pigment incorporated into liposomes of 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC), micelles and pre-micelle media of the detergent n-dodecyltrimethylammonium chloride (DTAC), and mixed, spontaneous, DMPC-DTAC vesicles and micelles. Chl a oligomers were characterized by UV-visible absorption, steady-state and time-resolved fluorescence, and fluorescence lifetime imaging microscopy. Equivalent diameters of the colloidal structures were obtained by fluorescence correlation spectroscopy. In DMPC liposomes and DMPC-DTAC vesicles and micelles, three fluorescence lifetimes indicated the coexistence of Chl a monomers (≈5 ns) and oligomers (≈1-2 to ≈0.1 ns). The increase in DTAC amount, in the mixed system, induces a progressive solubilization of DMPC liposomes (from vesicles to micelles) and simultaneous disruption of Chl a aggregates; in pure DTAC micelles, mostly monomers were found. The present work aims for a better understanding of chlorophyll-chlorophyll (Chl-Chl), Chl-lipid, and Chl-detergent interactions in spontaneous colloidal micro- and nanostructures.

THE NEAR-MID-IR HOMO-LUMO GAP IN AMIDE LINKED PORPHYRIN-RHODAMINE DYADS
José A. B. Ferreira, Vanda V. Serra, Antonio Sanchez-Coronilla, Sónia M. G. Pires, Maria A. Faustino, Artur M. S. Silva, Maria G. P. M. S. Neves, José A. S. Cavaleiro and S. M. B. Costa

Novel amide linked porphyrin–rhodamine dyads yield utmost intense red-shifted electronic transitions beyond the near-infrared region.
DESWELLING AND ELECTROLYTE DISSIPATION IN FREE DIFFUSION OF CHARGED PAMAM DENDRIMERS
Emilio García-Fernández, Pedro M. R. Paulo.

The diffusion coefficient of charged PAMAM dendrimers was measured by fluorescence correlation spectroscopy in aqueous solution at submicromolar concentrations. The solution pH was varied for conditions ranging from a fully charged to neutral charge dendrimer to infer about electrostatic swelling in the dilute regime. The diffusion coefficient of generation G4 increases by as much as 20% between high and low charge conditions due to the combined effects of polyelectrolyte deswelling and loss of electrolyte dissipation. By taking into account the electrolyte dissipation in the friction factor, we have found that the observed deswelling corresponds to a change of hydrodynamic radius between 7–13% for generation G4 and about 12% for generation G7. Simulations of molecular dynamics of dendrimer G4 show that counterion uptake by the dendrimer structure upon full protonation induces a 16% increase of its radius of gyration. The change in dendrimer size is slightly larger than that previously reported from neutron scattering techniques, thereby suggesting that electrostatic swelling is more pronounced at dilute dendrimer concentration and low ionic strength. It is confirmed that even higher generations, which have more congested molecular structures, can experience some degree of conformational change in response to a change of the dendrimer charge density.

SOLVENT AND CONFORMATIONAL EFFECTS ON THE PHOTOPHYSICS OF A HOMOLOGOUS PROGRESSION OF N-TERMINATED PHENYLENEVINYLENE OLIGOMERS

A homologous series of $p$-phenylenevinylene oligomers (PPV)$_n$ (n=3, 4 and 5) with terminal dialkylamino groups have been synthesized, and characterized. The photophysical and solvatochromic properties of oligomers with three, four and five phenyl groups were investigated in solution through steady-state and time-resolved fluorescence. Comparison of the effect of chain length on the absorption and PL spectra shows that the increase of the oligomer size is consistent with an extension of the conjugation length, i.e., a red-shift is observed in the maximum absorption and emission wavelengths. The decrease of the solvent polarity leads to small shifts of the absorption spectra and large blue-shifts. Global analysis of the fluorescence decays collected at different emission wavelengths, are found to be bi-exponential, in toluene at room temperature. The longer time appears as a decay component at all emission wavelengths and decreases from 949 to 850 ps with increasing chain length. The shorter time component (19-26 ps) appears as a decay at the onset of the emission spectrum and as a rise-time at
longer wavelengths. In contrast with the behavior previously observed with PPV oligomers substituted on the phenyl rings, solvent and temperature dependence studies excluded the hypothesis of this being due to conformational relaxation of the initially excited oligomer into a more planar conjugation. Instead, this component is assigned to specific interaction between the oligomer main chain and the solvent. Temperature dependence of spectra is related to backbone conformational behavior, and information on this has been obtained by temperature dependence of multinuclear NMR studies coupled with molecular dynamics simulations, Møller-Plesset 2 and DFT calculations.

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***Reactivity of Pyrimidine on Clean Ru(0001): Experimental and Calculated Infrared Spectra***

Ana R. Garcia, Adelino M. Galvao, and Laura M. Ilharco

The chemical behavior of pyrimidine on the (0001) close-packed surface of a Ru single crystal was studied by reflection–absorption infrared spectroscopy (RAIRS) and by Hartree–Fock ab initio calculations. At 95 K, the spectra and theoretical simulations indicate molecular docking at fcc hollow sites, as a π-complex almost parallel to the surface. With increasing coverage, some η4 on-top docked species appear, and for a highly packed monolayer physically adsorbed pyrimidine, with some preferential orientation induced by the chemically bonded species, is also present. Subsequent physisorbed layers, randomly oriented, form as exposure increases. The behavior of adsorbed species with thermal activation is not coverage dependent: annealing a low temperature packed monolayer induces rearrangements toward a denser π-complex layer, at the expense of the other surface species, up to 130 K. At this temperature, a tilted intermediate and 2-pyrimidyl bonded to the surface by dehydrogenated C2 and one N, with loss of resonance, and oriented with the C-N bond tilted toward the surface are also proposed. 2-Pyrimidyl is stable between 130 and 180 K and starts desorbing or decomposing above this temperature. A multilayer formed at low temperature is stable up to 110 K and desorbs by annealing to 120 K. For higher temperatures, the composition of the surface layers is similar to that obtained from thermal activation of a dense monolayer. At 150 K, the surface adlayer has the same composition whether it results from an annealed low-temperature monolayer, an annealed multilayer, or a layer built above the stability limit of the multilayer. The relevance of the results obtained is based on the eventual extrapolation to the interactions of pyrimidinic ring molecules with ruthenium.
ELECTRODEPOSITION AND CHARACTERIZATION OF NICKEL–COPPER METALLIC FOAMS FOR APPLICATION AS ELECTRODES FOR SUPERCAPACITORS
S. Eugénio, T.M. Silva, M.J. Carmezim, R.G. Duarte, M.F. Montemor

Nickel–copper metallic foams were electrodeposited from an acidic electrolyte, using hydrogen bubble evolution as a dynamic template. Their morphology and chemical composition was studied by scanning electron microscopy and related to the deposition parameters (applied current density and deposition time). For high currents densities (above 1 A cm\(^{-2}\)) the nickel–copper deposits have a three-dimensional foam-like morphology with randomly distributed nearly-circular pores whose walls present an open dendritic structure. The nickel–copper foams are crystalline and composed of pure nickel and a copper-rich phase containing nickel in solid solution. The electrochemical behaviour of the material was studied by cyclic voltammetry and chronopotentiometry (charge–discharge curves) aiming at its application as a positive electrode for supercapacitors. Cyclic voltammograms showed that the Ni–Cu foams have a pseudocapacitive behaviour. The specific capacitance was calculated from charge–discharge data and the best value (105 F g\(^{-1}\) at 1 mA cm\(^{-2}\)) was obtained for nickel–copper foams deposited at 1.8 A cm\(^{-2}\) for 180 s. Cycling stability of these foams was also assessed and they present a 90 % capacitance retention after 10,000 cycles at 10 mA cm\(^{-2}\).

PH-SENSITIVE POLYMERIC PARTICLES WITH INCREASED INHIBITOR-LOADING CAPACITY AS SMART ADDITIVES FOR CORROSION PROTECTIVE COATINGS FOR AA2024
R.I.D. Snihirov, S. V. Lamaka, M.M. Cardoso, J. A.D. Condeço, H. E.C.S. Ferreira, M. F. Montemor

The present work contributes to the design of smart anticorrosive coatings for corrosion protection of AA2024. Smart coatings, based on waterborne formulations modified with additives with high loading capacity of corrosion inhibitors open new opportunities for increased corrosion protection. In this work, a water-based epoxy coating was modified with Eudragit pH sensitive particles. The particles are able to store a high amount of corrosion inhibitor (8-hydroxyquinoline) and to act as pH-sensitive reservoirs, dissolving at acidic pH values, releasing the stored inhibitor. The quantification of the loading capacity was determined by HPLC-MS/MS, using a methodology developed for this purpose. Electrochemical impedance spectroscopy (EIS) was used to discriminate the electrical parameters assigned to the barrier properties of the coating and to the corrosion inhibition ability of coatings modified with Eudragit particles. The self-healing ability in artificial defects was studied by localized electrochemical impedance spectroscopy (LEIS). The results highlight the use of Eudragit particles as pH-sensitive reservoir, its ability to store higher contents of inhibitor when loaded with 8-hydroxyquinoline, and its self-healing potential.
OPTICAL SENSORS FOR CORROSION DETECTION IN AIRFRAMES
P.G. Venancio, R.A. Cottis, R. Narayanaswamy, J.C.S. Fernandes

The use of sensors to detect aluminium corrosion in airframe structures could allow reducing significantly the maintenance costs of fleets. An appropriate sensor may detect corrosion at an early stage, when the removal of the corroded material from the original structure does not involve a structural repair. More-over, by guaranteeing that corrosion is locally detected by an efficient sensor, the need for inspections in some areas could be eliminated or, at least, inspection intervals could be increased, with significant reduction of costs but still maintaining a conservative approach for aircraft safety. In the present work an optical sensor is presented, that can be used to detect corrosion products inside critical aircraft joints which are known to be very susceptible to corrosion. This sensor is based on the remote detection of aluminium ions produced in the corrosion process. The proposed method for the preparation of these sensors and the results obtained are discussed.

EFFECTS OF MECHANICAL FORMING ON THE CORROSION OF ELECTROGALVANIISED STEEL
A.C. Bastos, M.G.S. Ferreira, A.M.P. Simões

This paper presents a morphological and electrochemical characterisation of electrogalvanised steel (EG) and phosphated electrogalvanised steel (PEG) after plastic deformation. Previous investigations focused on the deformation of a coil-coating with the same substrates. The effect of forming on the complete system is known but not its influence on the individual layers. The study now reported used SEM to analyse the surface changes of EG and PEG after uniaxial and biaxial deformation and EIS and SVET to characterise the corrosion of the samples when immersed in 0.1 M NaCl.

**H⁺-SELECTIVE MICROELECTRODES WITH OPTIMIZED MEASURING RANGE FOR CORROSION STUDIES**

E.A.Zdrachek, A.G.Karotkaya, V.A.Nazarov, K.A.Andronchyk, L.S.Stanishevskii, V.V. Egorov, M.G.Taryba, D.Snihirova, M.Kopylovich, S.V.Lamaka

Two newly synthesized H⁺-selective ionophores: 2,3,4-tris(dodecyloxy)benzyldihexylamine and benzyldioctadecylamine, and six nitro-group containing solvents (2-nitrophenyloctyl ether, 2-nitrophenyl pentyl ether, 2-nitrophenyl phenyl ether, 1,2-dimethyl-3-nitrobenzene, 2-fluorophenyl 2-nitrophenyl ether, benzyl 2-nitrophenyl ether) were investigated to develop a membrane for glass-capillary H⁺-selective microelectrode with optimized measuring range for corrosion studies. It was shown that the microelectrode based on benzyldioctadecylamine and potassium tetra-kis(4-chlorophenyl) borate as anionic site dissolved in 2-nitrophenyloctyl ether possessed the best working pH range (2.6 – 12.3), Nernstian slope (55.0 mV decade⁻¹) and good time-related characteristics (potential drift 0.06 mV·h⁻¹, potential reproducibility ±0.1 mV and response time). It was successfully applied for pH measurements over corroding cut-edge samples of metallic coated steel using scanning ion-selective electrode technique.


**LOW-ENERGY ION SCATTERING SPECTROSCOPY OF SILICATE GLASS SURFACES**

Rui M. Almeida, Ray Hickey, Himanshu Jain, Carlo G. Pantano

Low-Energy Ion Scattering (LEIS) spectroscopy is a technique with a unique sensitivity to the elemental composition of the surface top atomic layers of a solid. LEIS measurements of simple binary silicate glasses with Na₂O, Cs₂O or BaO have shown differences in composition between the as-cast glass surface and the vacuum-fracture surface. The as-cast surface is usually depleted of modifier ions compared to the bulk glass composition, while the fracture surface is typically enriched with the monovalent modifier species, but not the divalent barium. While the melt surface depletion can be attributed to evaporation from the hot melt surface, the origin of the strong accumulation of the alkali on the fracture surfaces is probably due to their preferential migration to the glass surface during fracture. This phenomenon, immediately followed by surface rearrangement, is aided by the strain energy released, the heat generated near the crack tip during fracture and the shielding of the negative charge on the silicate tetrahedra by the alkali cations. The Si/O ratio shows usually little deviation from the nominal value.
Erbium-doped germanotellurite glasses and glass-ceramics have been prepared. Several crystalline phases could be distinguished in the X-ray diffraction patterns. The 1.5 \( \mu \text{m} \) photoluminescence (PL) emission of Er\(^{3+}\) (\(^4I_{13/2} \rightarrow ^4I_{15/2}\)) was studied in the glasses and glass-ceramics and the latter revealed an increase in the bandwidth of the PL spectra, compared to the PL peak of the starting glasses. Some heat-treated compositions present Stark splittings, indicating that the environment around Er\(^{3+}\) changed from an amorphous to a more ordered structure. Extended X-ray Absorption Fine Structure spectroscopy measurements were performed to investigate the Er\(^{3+}\) coordination before and after heat treatments. The glasses had a single coordination shell around Er\(^{3+}\), composed of oxygen, while two shells could be distinguished for the heat treated samples: a first oxygen shell for all heat-treated glasses and a mixed second nearest neighbor shell of Te and Er, for Te-rich compositions and of Ge and Er, for Ge-rich ones.
Thermodynamics of Fluids & Nanosystems
USING 129XE NMR TO PROBE THE STRUCTURE OF IONIC LIQUIDS

Pedro Morgado, Karina Shimizu, José M. S. S. Esperança, Patricia M. Reis, Luis Paulo N. Rebelo, José N. Canongia Lopes, Eduardo J. M. Filipe

The mesoscopic structure of 30 distinct ionic liquids was probed by 129Xe NMR spectroscopy. The interpretation of the experimental data was complemented using molecular dynamics results. The results clearly show that xenon can effectively probe the various environments characteristic of different ionic liquids (ILs) and is thus able to distinguish between distinct ionic liquid families, including different types of interactions with diverse types of anion/polar networks. A finer analysis of the NMR data also confirmed that the xenon probes can also provide information on how the complex structure of an IL evolves along a homologous series.

NANO-SEGREGATION IN IONIC LIQUIDS: SCORPIONS AND VANISHING CHAINS

Karina Shimizu, Carlos E. S. Bernardes, Alessandro Triolo, José N. Canongia Lopes

The present study analyses the large structural differences, first observed using X-ray diffraction, between 1-alkyl-3-methylimidazolium-based ionic liquids, [Cn mim][Ntf2] (n = 3, 6, 9), and their counterparts with ether-substituted alkyl side chains, [(C1OC1)(n/3)mim][Ntf2] (n = 3, 6, 9). The MD simulations—obtained using a non-polarizable atomistic force-field to model the ionic liquids under discussion—demonstrate that the suppression of the nanostructured nature in the ionic liquids with ether chains is persistent along the entire series and it is not due to any modification of the polar network of the ionic liquid but rather due to the different morphologies of the non-polar regions that surround it. The modification of the non-polar regions—shift from bulky segregated domains in [Cn mim][Ntf2] to thin enveloping ones in [(C1OC1)(n/3)mim][Ntf2]—are caused by the inability of the oxygen-substituted alkyl side chains to pack effectively side by side, the existence of kinks along the chain that lead eventually to intramolecular, scorpion-like interactions between the chains and the imidazolium ring, and by their stronger interactions with the cations of the polar network via the lone electron pairs of the ether oxygen atoms.
CATION ALKYL SIDE CHAIN LENGTH AND SYMMETRY EFFECTS ON THE SURFACE TENSION OF IONIC LIQUIDS


This work reports experimental measurements of the surface tension of two extended series of ILs, (symmetrical and asymmetrical cations) and their dependence with temperature. For both series the surface tension decreases with an increase in the cation side alkyl chain length up to aliphatic chains equal to hexyl. For ILs with longer aliphatic moieties the surface tension displays an almost constant behavior. These constant values converge to the surface tension values of long chained \( n \)-alkanes, indicating that, for sufficiently long alkyl side chains, the surface ordering is strongly dominated by the aliphatic tails present in the IL. The enthalpies and entropies of surface were also derived and the critical temperatures were estimated from the experimental data. Finally, the structure of a long-alkyl side chain IL at the vacuum-liquid interface was also explored using Molecular Dynamics simulations.

A BIOREFINERY FROM NANNOCHLOROPSIS SP. MICROALGA – EXTRACTION OF OILS AND PIGMENTS. PRODUCTION OF BIOHYDROGEN FROM THE LEFTOVER BIOMASS


The microalgae Nannochloropsis sp. was used in this study, in a biorefinery context, as biomass feedstock for the production of fatty acids for biodiesel, biohydrogen and high added-value compounds. The microalgal biomass, which has a high lipid and pigment content (mainly carotenoids), was submitted to supercritical CO\(_2\) extraction. The temperature, pressure and solvent flow-rate were evaluated to check their effect on the extraction yield. The effect of adding a co-solvent (ethanol) was also studied. When supercritical CO\(_2\) doped with 20\% (w/w) ethanol was used, it was possible to extract with higher yields. Furthermore, the remaining biomass after extraction was effectively used as feedstock to produce biohydrogen through dark fermentation by Enterobacter aerogenes resulting in hydrogen production with interesting yields.
MOISTURE ABSORPTION IN IONIC LIQUID FILMS
José Restolho, José L. Mata, Rogério Colaço, Benilde Saramago

The uptake of water vapor by ionic liquids (ILs) has been studied by various research groups, but there is little knowledge on how liquid confinement affects the process of moisture absorption. In this work, several imidazolium-based ILs deposited on quartz crystals were used as water vapor sensors in a high sensitivity quartz-crystal microbalance with dissipation. The process of water vapor absorption by the IL films was interpreted, taking into account the changes of the different harmonics of the fundamental frequency. For the most viscous ILs, the decrease in viscosity was the dominant effect, while for the others, the mass loading effect predominated. However, there are differences within the latter set: a gradual water adsorption and diffusion was observed in some films; in contrast, a discontinuity seems to have occurred between the formation of a water film on top of one of the ILs film and its diffusion into the bulk. The kinetics of water absorption in the films of acetate-based ILs was well described by a two-step model, and water diffusion coefficients in those films were obtained.

VISCOSITY MEASUREMENTS OF THREE IONIC LIQUIDS USING THE VIBRATING WIRE TECHNIQUE
João C. F. Diogo, Fernando J. P. Caetano, João M. N. A. Fareleira, William A. Wakeham

Recently we have started to study the applicability of the vibrating-wire technique to the measurement of the viscosity of ionic liquids. The fact that these liquids are electrical conductors represents a source of additional experimental uncertainty, if a bare metallic wire is used as a sensor. A previous study showed that the effect of the electrical conductivity was essentially insignificant. The current study extends our work to ILs which have an order of magnitude higher electrical conductivity than the ones used previously. Although the main aim is the study of the effect of the electrical conductivity on the performance of the vibrating wire technique, it must be also stressed that one of the ILs [C₆mim][NTf₂] has been selected as an IUPAC reference fluid.
This book is the outcome of remarkable contributions from the renowned experts in the field of nanofluids and covers the entire spectrum of nanofluids starting from their preparation and various properties to potential applications. As an emerging field and having fascinating thermophysical and heat transfer properties as well as highly demanding numerous applications nanofluids have sparked immense interest worldwide and have been a subject of explosion of research in recent years which can be evidenced from the large number of nanofluids related research publications. Besides the state-of-art reviews and critical analysis on numbers of key areas of nanofluids this book presents comprehensive experimental and theoretical research efforts on the thermal conductivity, viscosity, convective heat transfer, capillary wetting, and transport properties of nanofluids. Study on application of nanofluids in microfluidic technology is presented and another new area of nanofluid-based optical engineering has also been explored. Featuring contributions from some of the leading researchers in the field this book is a unique reference source and invaluable guide to scientists, researchers, engineers, industrial people, graduate and postgraduate students and academicians across the science and engineering disciplines.


**THERMO-PHYSICAL PROPERTIES OF IONIC LIQUID DICYANAMIDE (DCA) NANOSYSTEMS**


IoNanofluids have emerged as a possible alternative to current engineering fluids for heat transfer applications, namely in small volume heat exchangers and micro-channels. Thermal conductivity and density play a crucial role for the chemical plant design of green processes. Existing data are very scarce and inaccurate, mostly affected by impurities and the presence of water in the ionic liquids. In the present paper, we report new data on the thermal conductivity and density of [C₄mim][dca], [C₂mim][dca] and [C₄mpyr][dca] at temperatures between (293 and 343) K at $p = 0.1$ MPa and IoNanofluids based on them with MWCNTs, in order to understand the effect of adding nanomaterials to a ionic liquid matrix and modification of its heat transfer mechanism. Discussion about the effect of the cation, its side alkyl chain, head group and anion structure in the properties studied concluded that it is essential to understand better the mechanism of heat transfer in these systems, namely the role played by the interface ionic liquid-nanoparticle, whatever molecular shape the ions have. Current theories used to calculate the thermal conductivity enhancement are insufficient to predict its value and variation with volume fraction of the nanomaterial.
AN EFFICIENT CU (II)-BIS(OXAZOLINE)-BASED POLYMER SUPPORTED IONIC LIQUID PHASE CATALYST FOR ASYMMETRIC CARBON-CARBON BOND FORMATION

Simon Doherty, Julian G. Knight, Jack R. Ellison, Peter Goodrich, Leanne Hall, Christopher Hardacre, Mark Muldoon, Ana Ribeiro, Maria J.V. Lourenço, Carlos A. Nieto de Castro, Paul Davey and Soomin Park

The concept of immobilising an ionic liquid in the form of a cation-decorated polymer, e.g. in the form of a polyelectrolyte, to combine the favourable properties of ionic liquids with the advantages of heterogenisation as well as overcome leaching and improve long term stability in asymmetric catalysis has been explored. The asymmetric Diels–Alder reaction between N-acryloyloxazolidinone and cyclopentadiene and the Mukaiyama-aldol reaction between methylpyruvate and 1-phenyl-1-trimethylsilyloxyethene have been catalysed by heterogeneous copper(II)-bis(oxazoline)-based polymer immobilised ionic liquid phase (PIILP) systems generated from a range of linear and cross linked ionic polymers. In both reactions selectivity and ee were strongly influenced by the choice of polymer. A comparison of the performance of a range of Cu(II)-bis(oxazoline)-PIILP catalyst systems against analogous supported ionic liquid phase (SILP) heterogeneous catalysts as well as their homogeneous counterparts has been undertaken and their relative merits evaluated.

SUPERIOR THERMAL FEATURES OF CARBON NANOTUBES BASED NANOFLOIDS- A REVIEW

S. M. Sohel Murshed and C. A. Nieto de Castro

Recent progresses in research on several key thermal features and potential applications of carbon nanotubes-laden nanofluids are reviewed and addressed. Besides briefing on the preparation of these nanofluids, available studies on conduction, convection and boiling heat transfers of this specific class of nanofluids are discussed in detail. Effects of different parameters such as concentration of carbon nanotube and temperature on thermal conductivity, convective heat transfer coefficient, and boiling critical heat flux are also demonstrated. It is found that despite inconsistencies among available data and inconclusive heat transfer mechanisms, substantial increase in these thermal features of carbon nanotubes-nanofluids compared to their base fluids remain undisputed. In addition to the work on specific heat and thermal diffusivity, available theoretical models and heat transfer mechanisms of this particular type of nanofluids are presented and discussed. Research on a new class of nanofluids termed as “ionanofluids” is also reported. Review reveals that ionanofluids exhibit superior thermal properties compared to their base ionic liquids and these properties further increase with increasing concentration of carbon nanotube as well as fluid temperature to some extent. Carbon nanotubes based both nanofluids and ionanofluids show great potential as advanced heat transfer fluids in many important applications.
Thermodynamic properties of (amphiplile + water) mixtures have been largely studied since they have been showing interesting features, mainly in the water-rich region. The water activity was evaluated in 39 mixtures of water with 1-propoxypropan-2-ol (1-pp-2-ol) at $T = 298.15 \text{ K}$ using an indirect method which measures the system capacitance. A careful calibration of the apparatus and the many measurements in the water very-rich region have enabled the determination of activity coefficients of 1-pp-2-ol using the Gibbs–Duhem equation, the system being modelled using a 6-suffix Margules equation. Infinite dilution activity coefficients for the two components are presented together with their associated uncertainties. Excess molar Gibbs free energies were estimated and compared with literature values for the aqueous system of 2-butoxyethanol, which is a structural isomer of 1-pp-2-ol.

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**HIGH-TEMPERATURE VAPOR-LIQUID EQUILIBRIUM FOR THE WATER-ALCOHOL SYSTEMS AND MODELING WITH SAFT-VR: I. WATER-ETHANOL**


Linear alcohols represent an important alternative source of energy. The design of industrial processing equipment of these alcohols needs accurate vapour–liquid equilibrium (VLE) measurements of binary mixtures with water at high temperatures. A flow apparatus was built to carry out vapour–liquid equilibrium at high temperatures for water–alcohol binary mixtures in the temperature range of 363–443 K and pressures up to 1.7 MPa. Experimental VLE data are presented for water–ethanol system for temperatures between 363.3 and 423.7 K, and pressures up to 1 MPa and compared with available literature data. Its performance was found to be commensurate with the design parameters and the required accuracy. The statistical associating fluid theory for potentials of variable range (SAFT-VR) was used to correlate the data. The phase equilibria for this system are accurately described with this approach, especially considering that the parameters were obtained for a shorter region of the phase diagram.
Nanomaterials have widely been obtained from synthetic sources. Natural compounds have structures and properties that can possibly replace some of the environmentally dangerous compounds. Melanins are widely distributed in living organisms. They act mainly as photo-protectors. The capacity of these biopolymers to convert radiative energy into heat stimulated our curiosity about its structural, chemical and thermophysical properties, regarding possible thermal applications. The search for new materials with high heat storage capacity for energy recovery and efficiency increase in domestic and industrial applications, lead us to study this properties in melamins, namely natural melanin subjected to different pre-treatments and synthetic melanin using solid state techniques, and trying to establish a relationship between their composition, structure and morphology. Additionally the behaviour of both types of melamins when exposed to heat and UV-Vis radiation was also studied. This paper shows that natural melamins have high potential, either in the solid form for heat storage or suspended in ionic liquids (IoNanofluid) for advanced heat transfer fluids, biodegradable and environment-friendly.

The NVT-Molecular Dynamics Model performs molecular dynamics simulations at constant temperature of 32, 108, 256 or 500 molecules interacting through the Lennard-Jones potential, in a wide range of densities and temperatures covering liquid, vapour and solid states. Thermodynamic properties, radial and speed distribution functions, velocity autocorrelation functions (vcf's) and their Fourier spectra, and mean square displacements (msd's) are calculated and displayed. Self-diffusion coefficients are worked out from the vcf's and msd's. Self-space-time correlation functions (stc's) are estimated and compared with the Gaussian approximation. The 3D molecular motions can also be visualized. The motion equations are integrated by two methods, at user's choice: the damped-force with leap-frog Verlet's algorithm, and the "ad-hoc" rescaling with the velocity Verlet algorithm. The model allows assessing the role of the potential cut-off distance, the number of steps in equilibration runs, the time-step and the gap between time origins for vcf's, msd's and stc's. The NVT-Molecular Dynamics Model was developed using the Easy Java Simulations (EJS) modelling tool. It is distributed as a ready-to-run (compiled) Java archive. Double clicking the jar file will run the program if Java is installed.
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