FROM THE LITERATURE

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♦ A Commentary [A. Klamt *et al., Acc. Chem. Res.*, 2009, **42**, 489], contributed by several European research institutions, including the Università di Pisa, and the University of Toronto, has appeared comparing their solvation model SM8 with other competing models. ♦ On this subject, mention should also be made of the adjacent Commentary by C.J. Cramer *et al*. [*Acc. Chem. Res.*, 2009, **42**, 493], further to their paper on a solvation model appeared earlier [C.J. Cramer, *Acc. Chem. Res.*, 2008, **41**, 760].

♦ S. Aime of the Università di Torino is Guest Editor, together with T.J. Meade of Northwestern University of a special issue of *Acc. Chem. Res.*, July 2009, dedicated to the Chemistry of Molecular Resonance Imaging (MRI). ♦ The same issue hosts an article by S. Aime *et al*. [*Acc. Chem. Res.*, 2009, **42**, 822] which describes the use of two important systems used in MRI, namely the gadolinium complexes and the new emerging class of chemical exchange saturation transfer agents.

An intense research activity has appeared on metal oxides, with special attention to their preparation and applications. ♦ A contribution [A. Grabulosa *et al*., *Inorg. Chem.*, 2009, **48**, 8031] from the Università di Ferrara in collaboration with the Université de Nancy and the Université Paul Verlaine, Metz, has reported a homoleptic cationic complex of ruthenium(II), of formula $[Ru(L)_3]^{2+}$, isolated as the hexafluorophosphato derivative, where L denotes a 2,2'–dipyridyl ligand containing two different substituents in the 4,4' positions. The compound was characterized and used to sensitize TiO_2 for applications in solar cells. ♦ As a matter of fact, surfaces of TiO_2 have been used for their photocatalytic properties. A paper contributed by the Universities of Milano–Bicocca, Milano, Cagliari and Venezia [R. Scotti *et al*., *Chem. Mater.*, 2008, **20**, 4051] has reported the sol–gel synthesis of TiO_2 by hydrolysis of $TiCl_4$ in the presence of a polyether triblock copolymer. By calcination, mesoporous and nanocrystalline TiO_2 was obtained, as characterized by conventional surface techniques (TEM, HRTEM, XRD, area measurements). ♦ In a preceding report, activity in a similar area has been reported. A patent assigned to Italcementi SpA, Bergamo, Italy [inventors: L. Cassar and C. Pepe, US Patent No. 6,117,229; Sept. 12th 2000] describes the formation of a cement characterized by a high capacity of reflecting sunlight with a minimum degree of absorption. The preferred photocatalyst is titanium dioxide, usually as its anatase modification. ♦ A contribution from INSTM at the Università di Sassari, in collaboration with other institutions in Argentina [L. Malfatti *et al*., *Chem. Mater.*, 2008, **21**, 2763] has reported a simplified method to produce porous thin films of TiO_2 by controlled self–assembly, swelling and phase separation, in the presence of both polypropylene glycol and a templating agent, starting from $Ti(OBu)_4$ prepared *in situ*. ♦ The collaboration of a CNR Istituto per la Microelettronica ed i Microsistemi (IMM) located in Lecce [M. Epifani *et al*., *Chem. Mater.*, 2009, **21**, 862] has produced metal oxide sols of several metals through hydrolysis of their precursors, namely chloro–alkoxo– or acetylacetonato derivatives. Metal oxide particles were obtained by heating the precursors in a system constituted by tetradecene and an aliphatic amine. The formation of the nanoparticles is influenced by both the nature of the amine and the method of processing the original sol. ♦ Researchers of the Università di Cagliari in collaboration with colleagues operating at the British SuperSTEM Laboratory in Daresbury [D. Carta *et al*., *Chem. Mater.*, 2009, **21**, 945] have studied some highly porous silica aerogels, containing iron and cobalt or iron and nickel, as intermediates in the formation of $CoFe_2O_4/SiO_2$ and $NiFe_2O_4/SiO_2$, respectively. ♦ Highly photoluminescent silica layers doped with europium(III) or thorium(III) were reported [S. Quici *et al*., *Chem. Mater.*, 2009, **21**, 2941], as a contribution from the Università di Milano, the ISOF–CNR Institute of Milano, the Università di Padova and the Università di Bari. The molecular precursors were anchored on silica by the sol–gel technique. The luminescence showed an increase with respect with the corresponding systems in aqueous solution. ♦ A contribution from the University of Utrecht [A.F. Demirörs *et al*., *Chem. Mater.*, 2009, **21**, 979] reports the synthesis of titania/silica core–shell particles by coating titania particles with silica. If the TiO_2 particles are treated with silica prior to drying, titania–silica spheres are produced with a uniform distribution of the two oxides.

♦ The Università di Cagliari, in collaboration with the Università di Firenze and the Universities of Nottingham and Southampton [M. Mameli *et al*., *Inorg. Chem.*, 2009, **48**, 9236] has described two new quinoline pendant–arm derivatives and their metal complexes. The potentiometric data show that the affinity of these systems decreases in the following order of metal(II) cations: Cu>Zn>Hg>Pb>Cd.

♦ Syndiotactic polystyrene films have been subjected to a sulfonation procedure [A. Borriello *et al*., *Chem. Mater.*, 2009, **21**, 3191] as for a contribution from the Universities of Napoli and Salerno: sulfonation of the aromatic rings was easily achieved with the amorphous phase, while the δ–form is preserved. ♦ A contribution from the Università di Salerno [A.R. Albunia *et al*., *Chem. Mater.*, 2009, **21**, 3370] reports on the studies regarding the ε–phase of syndiotactic polystyrene (s–Ps) characterized by channel–shaped porosity. Three uniplanar orientations of co–crystalline films of s–Ps have been detected and found to be controlled by solvent–induced crystallization and by thermal treatment.

♦ A paper contributed by several research institutions located in Bari, Lecce, Palermo and Milano–Bicocca [T. Placido *et al*., *Chem. Mater.*, 2009, **28**, 5382] reports the photochemical synthesis of gold nanorods in an aqueous medium, and in the presence of Ag^+ ions. The role played by silver in the growing process of gold particles has been pointed out.

♦ Some new five–electron donor ligands have been reported as a

contribution from the Università di Bologna [S. Bordoni *et al*., *Organometallics*, 2009, **28**, 5382]. This paper has described the properties of some new carbonyl derivatives of rhenium(I) containing a novel class of alcohol– and ether–functionalized indenyl ligands.

♦ Two complexes of $ZnCl_2$ containing heteroscorpionato ligands have been synthesized [S. Milone *et al*., *Inorg. Chem.*, 2009, **48**, 9540], as for a contribution from the Universities of Salerno and Ferrara. The complexes contain a tetrahedral zinc centre coordinated to the imino nitrogens of the pyrazolyl rings. Association constants of about 10^3 M^{-1} were measured in $MeOH/H_2O$ solution.

♦ B. Ventura *et al.* of ISOF–CNR in Bologna [*Inorg. Chem.*, 2009, **48**, 6409] have contributed, in collaboration with the Université de Strasbourg, to the preparation of a cationic platinum(II) complex containing a trisubstituted (with ^{t}Bu groups) terpyridine and linked to a delocalized unsaturated system constituted by a phenylacetylide residue further connected to fullerene C_{60}. The electrochemistry of this system shows that the first reduction process is fullerene–based.

♦ The Universities of Sassari, Milano and Torino collaborated in the synthesis of cyclometalated complexes of palladium(II) and platinum(II) [A. Zucca *et al*., *J. Organometal. Chem.*, 2009, **694**, 3753], derived from 6,6'–diphenyl–2,2'–bipyridine, by reaction with Na_2PdCl_4 or Na_2PtCl_4. Chloride removal by $AgBF_4$ in the presence of CO or PPh_3 gives the corresponding cationic species, as the tetrafluoborato derivatives.

♦ A group of the Università di Trieste, in collaboration with institutions operating in India [A. Banerjee *et al*., *Inorg. Chem.*, 2009, **48**, 8695] has reported three new dinuclear complexes of zinc(II) with new compartmental 18–membered macrocyclic ligands. The complexes were reported to have an inhibitory effect on cell proliferation of human cancer. ♦ A paper contributed by the Dipartimento di Scienze Farmaceutiche, Università di Padova and by some research institutions located in Lisbon [A.P. Ferreira *et al.*, *Organometallics*, 2009, **28**, 5412] has described some new organometallic benzo[*b*]thiophene derivatives. For instance, 2–benzoyl–3–ferrocenylbenzo[*b*]thiophenes with the benzoyl substituent containing tertiary alkylimino groups are expected to have affinity for the estrogen receptor.

♦ Corrolates (containing a modified porphyrin system) of silver(III) have been reported as a contribution of the Università di Roma "Tor Vergata", in collaboration with Louisiana State University [M. Stefanelli *et al*., *Inorg. Chem.*, 2009, **48**, 6879]. Aimed at studying the demetalation behaviour, cyclic voltammetry was applied on some of the derivatives in pyridine, and the demetalated product was spectrophotometrically characterized.

♦ A paper contributed by the University of Ottawa [L. Maretti *et al*., *J. Am. Chem. Soc.*, 2009, **131**, 13972] has reported the preparation of highly fluorescent silver nanoparticles obtained by contacting $Ag(CF_3COO)$ with a source of ketyl radicals, namely 1–[4–(2–hydroxyethoxy)phenyl]–2–hydroxy–2–methyl–1–propan–1–one. The trifluoroacetato ligand was established to be necessary for the preparation of a highly fluorescent material, cyclohexylamine being used as the reducing agent, in toluene as medium. The particles thus obtained showed a strong luminescence in the visible region. The maximum of the emission was observed at 528 nm in toluene. The presence of the trifluoroacetato was found to be essential for highly fluorescent particles. It is interesting to note that also the dialkylcarbamato derivatives of silver are dinuclear, as reported in contributions from the Università di Pisa [D. Belli Dell'Amico *et al.*, *Chem. Rev.*, 2003, **103**, 3857, and refs. therein].

♦ Mesostructured silica films [P. Innocenzi *et al.*, *J. Mater.*, 2009, **21**, 2555] have been the subject of a review–article contributed by the Università di Sassari, in collaboration with the Australian CSIRO: the Evaporation–Induced Self–Assembly (EISA) has been highlighted as a frequently used method.

♦ A paper contributed by both the University and the Technical University of Wroclaw [P. Sobota *et al.*, *Inorg. Chem.*, 2009, **48**, 6584] has appeared describing heteronuclear chloro–alcoholato (L) derivatives containing the Ca/Ti, Ca/Zr, Sr/Ti and Mn/Ti systems. The X–ray crystal structure of several compounds were reported including the hetero–octanuclear $Mn_4Ti_4(\mu\text{–}Cl)_2(\mu_3,\eta^2\text{–}L)_2(\mu,\eta^2\text{–}L)_{10}Cl_6$ containing both metal cations in the oxidation states III and II. In this context, polynuclear derivatives are often encountered in the area of *N,N*–dialkylcarbamato ligands, [D. Belli Dell'Amico *et al.*, *Chem. Rev.*, 2003, **103**, 3857, and refs. therein]: for example, the hexanuclear compound $Mn_6(O_2CNEt_2)_{12}$ of manganese(II) was established crystallographically to consist of a central core of four five–coordinated manganese atoms in an approximately trigonal bipyramidal geometry, the remaining two manganese atoms displaying a distorted octahedral geometry. The manganese derivative was found to be isostructural with the corresponding cobalt(II) derivative.

♦ A contribution from the Università di Perugia, in collaboration with Northwestern University has described the preparation and properties of two low–dimensional polyacetylene derivatives [A. Marrocchi *et al.*, *Chem. Mater.*, 2009, **21**, 2592]: one of the compounds contains an anthracene core linked to two ethynylene–phenylene moieties attached at the 9,10–positions of the condensed aromatic hydrocarbon. In the other compound the central core of the former system is replaced by a thiophene–benzothiadiazole–thiophene system. The electrochemical and optical properties of these products were evaluated.

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