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The proximity of Pt in NO_x storage-reduction catalysts

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Automobile emission can be limited using NO_x storage reduction (NSR) catalysts typically containing Pt/Ba/Al₂O₃. Pt is essential for NO oxidation and NO_x reduction in such catalysts. Here, the effect of Pt proximity to the Ba storage sites was investigated on catalysts with preferential Pt location on Al or on Ba (Fig 1.) produced by a twin flame spray pyrolysis (FSP) unit. The spillover and support effect was elucidated by comparing Pt/Ba/Al₂O₃ with Pt/Ba/CeO₂. The best catalyst performance was found for materials with Pt near the Ba [1].

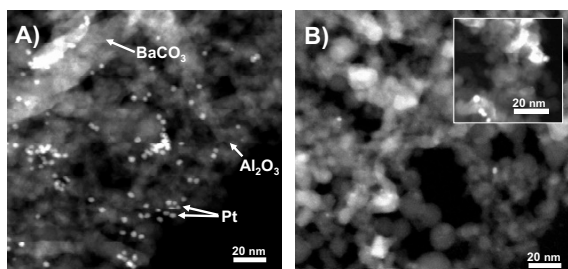


Figure 1: Pt/Ba/Al₂O₃ catalysts with Pt preferentially on Al₂O₃ in A) and Pt on BaCO₃ in B).

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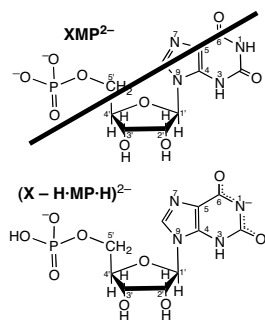
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Xanthosine 5'-Monophosphate (XMP). Coordinating Properties of a Chameleon-like Nucleotide

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Xanthosine and its nucleotides are important metabolic intermediates and thus widely studied [1]. Unfortunately, the structure of the monophosphate commonly shown in textbooks depicts XMP²⁻ and this is not correct: (i) XMP²⁻ is a minority tautomer that occurs only to about 10%; the dominating one (90%) is (X - H·MP·H)²⁻ which carries a proton at the phosphate group but has lost one from the (N1)H/(N3)H sites, thus giving rise to further ambiguities [2]. (ii) Most importantly, in the physiological pH range of about 7.5 XMP is present as the 3-fold negatively charged (X - H·MP)³⁻ species!



The two most relevant complexes formed with divalent metal ions (M²⁺) are (M·X - H·MP·H)⁺ and (X - H·MP·M)⁻ [2]. In the first case M²⁺ is N7-coordinated, forming to about 65% outersphere macrochelates with the P(O)₂(OH)⁻ group; note, the given formation degree is independent from the kind of metal ion involved. In contrast, in the (X - H·MP·M)⁻ complexes the primary M²⁺ binding site is the PO₃²⁻ group and macrochelates form in this case innersphere with N7, the formation degree being strongly dependent on the kind of M²⁺ involved, e.g., being 0% with Mg²⁺, 50% with Mn²⁺, and 90% with Zn²⁺ [2].

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[1] Review: E. Kulikowska, B. Kierdaszuk, and D. Shugar, *Acta Biochim. Polonica*, **2004**, *51*, 493–531.

[2] H. Sigel, B. P. Operschall, and R. Griesser, *Chem. Soc. Rev.* **2009**, *38*, in press.

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Self-organized liquid-crystalline dendrimer-functionalized gold nanoparticles: a promising optical hybrid material

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Our study focuses on the synthesis of well-defined gold nanoparticles (AuNPs) bearing liquid-crystalline (LC) dendrimer ligands in their shell, combining ligand exchange^[1] and chemical ligand modification.^[2]

Functionalization using thiolated dendrimers seems the easiest way to obtain these materials; however, large amounts of ligand are required in this case.^[3] An alternative is the synthesis of tailored OH-functionalized AuNPs prior to the possible chemical reaction with the LC dendritic carboxylic acids.



These composites which self-organize^[3] are promising candidates to build up artificial three-dimensional structures with unique properties (metamaterials).^[4]

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Synthesis of ditopic 2,2':6',2''-terpyridine ligands and their Fe(II) and Ru(II) complexes.

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The {M(tpy)₂}ⁿ⁺ (tpy = 2,2':6',2''-terpyridine) motif is increasingly used in preference to {M(bpy)₃}²⁺ (2,2'-bipyridine) domains in supramolecular chemistry.[1] One major reason is that {M(bpy)₃}²⁺ is chiral and the incorporation of multiple centres gives rise to diastereoisomeric structures. This is not to say that {M(tpy)₂}ⁿ⁺ motifs cannot be chiral; the commonest stereogenic factor is the desymmetrization of the ligand by substitution on one of the two terminal rings. We recently demonstrated that a symmetrical ligands linked through flexible chains can also give rise to chiral structures as a result of the "trapping" of the chain between tpy domains.[2]

We now describe the extension of these observations to new types of bis(2,2':6',2''-terpyridine) ligands and report the spectroscopic characterisation of atropisomeric complexes of these ligands and the investigation of the dynamic processes interconverting the enantiomers.

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[2] Chow, H.S.; Constable, E.C. and Housecroft, C.E. *Dalton Trans.* **2003**, 4568-4569.