

to fabricate crystalline undoped and doped ZnO namely the liquid phase epitaxy (LPE) of thin films on ZnO substrates (2) and synthesis of microcrystals from low-alkaline solutions using mild hydrothermal conditions(3). Photo- and radioluminescence spectra were measured at the undoped and doped with In, Ge, and Sb ZnO thin films and hydrothermal ZnO crystals respectively. The effect of doping, zinc source, and experimental parameters was studied on the phase composition, crystal morphology and size, and luminescence. Molecular imprinted polymer nanoparticles (nanoMIPs) are often referred to artificial receptors. Hybridmaterials based on doped hydrothermal ZnO nanocrystals and nanoMIPs are supposed to work as a specific, nontoxic, and multifunctional label for modern bio-analytics and diagnostics as well as in down stream processing in chemical and pharmaceutical industry.

References

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Keywords: hydrothermal, luminescence, hybridmaterials

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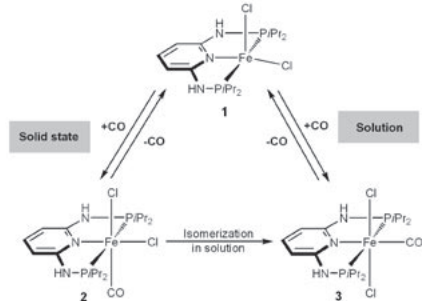
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Solid-state vs solution reactivity of iron complexes: Stereospecific and reversible CO binding

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Chemical transformations that occur in crystalline materials are very rare because most chemical reactions cause intramolecular reorganization, which typically results in the loss of crystallinity. We report here on novel solid-state (and solution) reactivities of iron complexes which maintain their crystallinity even upon CO uptake. When crystalline **1** is exposed to an atmosphere of CO, adsorption of the gas into the organoiron molecules was indicated by a color change of the material from light yellow to deep red, giving cis-[Fe(PNP)(CO)(Cl)₂] (**2**) as the sole product (Scheme 1). On the other hand, when CO was bubbled into a solution of **1** for two minutes, a blue solid precipitate was formed identified as the corresponding trans complex [Fe(PNP)(CO)(Cl)₂] (**3**). This process takes place stereospecifically and reversibly depending on the reaction conditions employed triggering changes in the color of the products, in the coordination geometry around the iron center, and in the spin states. Mechanistic aspects are discussed based on DFT calculations, solid-state NMR, and powder diffraction studies.



Keywords: gas sensors, CO binding, solid-state reactivity

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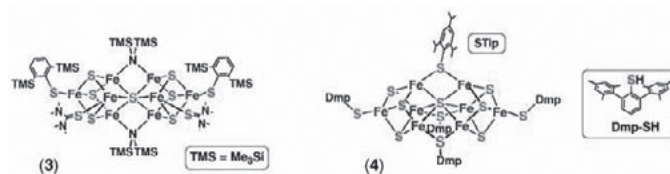
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A new synthetic route to iron-sulfide clusters modeling the active site of nitrogenase

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Recently, we developed a new method to synthesize Fe/S clusters, utilizing Fe{N(TMS)₂}₂ as the precursor. This route has allowed us to build Fe/S clusters in non-polar solvents, and resulted in a series of unprecedented cluster structures, which resemble closely the active sites of nitrogenase. We succeeded in reproducing the unusual [8Fe-7S] inorganic core structure of P-cluster (PN) of nitrogenase from a self-assembly reaction of Fe{N(TMS)₂}₂, SC(NMe₂)₂, HSTip, and S₈, which gave rise to [{N(TMS)₂}₂]{SC(NMe₂)₂}Fe₄S₃]₂(μ⁶-S){μ-N(TMS)₂}₂ (**1**). The cluster **1** consists of 6Fe(II)+2Fe(III) irons, while PN carries eight Fe(II)s. Although cluster **1** is unstable under the presence of thiols, it was possible to isolate (NEt₄)₂{N(TMS)₂}₂(SAr)Fe₄S₃]₂(μ⁶-S){μ-N(TMS)₂}₂ (**2**) and [(SAr){SC(NMe₂)₂}Fe₄S₃]₂(μ⁶-S){μ-N(TMS)₂}₂ (**3**) from careful treatments of (1) with corresponding thiolates and thiols. Yet another type of [8Fe-7S] cluster (**4**) was synthesized from the reaction of [Fe(Stip)]₂(μ-SDmp)₂ with S₈ in toluene, the structure of which links topologically FeMoco and P-cluster of nitrogenase and has an intriguing 5Fe(II)+3Fe(III) oxidation state with a doublet ground state.



Keywords: iron-sulfur cluster, nitrogenase, synthesis

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Advances in electrostatics and application to molecular reactivity

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Most important prerequisites for the reactivity of molecules are the prediction, interpretation and localization of the preferred sites of reactions. Molecular reactivity indicators generally correlate with the atomic charges, the molecular orbital densities and the electrostatic potential. Atomic bonding structures described in the theory of R.F.W. Bader gain acceptance in the field [1]. In this lecture, I will focus on the electrostatic potential, electric field and derived properties to rationalize the molecular interactions. The molecular surface of electrostatic potential defines the nucleophilic and electrophilic attack regions and the electric field assists in predicting the path of reactants in the vicinity of a molecule. The experimental approach of X-ray high resolution diffraction is used to derive these properties. Their computations are based on the Hansen-Coppens model of the electron density [2]. Molecular electrostatic potential

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