

Transformations of well-defined organozinc precursors towards materials with desired functionality

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The investigations carried out within the PhD thesis concern synthesis and characterization of alkylzinc hydroxides of the type of $[RZnOH]$ and $[(R)_xZn_y(L)_z(OH)_n]$ as well as their utilization as well-defined precursors of materials based on nanostructured ZnO and zinc carbonate building units. The integral part of the research was characterization of physicochemical properties of the obtained molecular entities and functional materials.

The first part of the thesis concerns synthesis and characterization of model *tert*-buthylzinc hydroxides. The application of di-*tert*-butylzinc as a starting reagent enabled isolation and structure determination (in the solid-state and in a solution) of alkylzinc hydroxide $[tBuZn(\mu_3-OH)]_6$ (**1₆**) and its adduct with 4-methylpyridine $[tBu_6Zn_6(\mu_3-OH)_4(\mu-OH)_2(py-Me)_2]$ (**2**).^[I,III] Compound **1₆** was further used for development of original synthetic strategy leading to mixed *tert*-butyl(*tert*-butoxy)zinc hydroxides containing $[tBuZnOH]$ and $[tBuZnOtBu]$ building units, $[(tBu)_4Zn_4(\mu_3-OtBu)_x(\mu_3-OH)_{4-x}]$ [**4**] if $x=3$; [**5**] if $x=2$; [**6**] if $x=1$.^[III]

The second and third part of the dissertation describes comprehensive investigations on temperature and mechanochemical transformations of obtained alkylzinc hydroxides, **1₆** and **4-6**, towards ZnO nanocrystals. The investigation showed that the Zn-OH groups appear to be a desirable feature for the solid-state synthesis of ZnO nanocrystals that significantly decreases the decomposition temperature of crystalline alkylzinc hydroxide precursors.^[III] Moreover we showed that **1₆** appears as an excellent precursor for mechanosynthesis of ZnO nanoparticles, which can be transformed in ZnO phase even at room temperature *via* grinding.

In the fourth part we describe comprehensive experimental investigations on: (i) step-by-step sequence of the reaction between **1₆** or **2** and CO₂, and (ii) the effect of a donor ligand and/or an excess of *t*Bu₂Zn as an external proton acceptor on the reaction course and structure of the resulting carbonates.^[III,IV] In this stage of the project we isolated and structurally characterized the first alkylzinc carbonate compound, $[(tBuZn)_2(\mu_5-CO_3)]_6$ (**8**), as well as a mesoporous material based on zinc carbonate nanoparticles.

In the last part we describe the application of the acquired knowledge for elaboration of the new type of complex precursors $[(R)_xZn_y(L)_z(OH)_n]$ and their usage for the synthesis of functional materials *via* chemical fixation of CO₂. As a result we isolated and characterized *inter alia* new *tert*-buthylzinc hydroxide derivative of 8-hydroksoquiniline (q-H), $[(tBu)_2Zn_4(q)_4(\mu_3-OH)_2]$ (**11**).^[VI] Compound **11** in the reaction with CO₂ leads to the formation of novel heteroleptic zinc carbonate-hydroxyquinolate nanoclusters, $[Zn(\mu_6-CO_3)]_4[Zn(q)_2]_6$ (**12**).^[VI] The non-covalently-driven self-assembly of single molecules of **12** leads to the formation of an unprecedented microporous, fluorescent noncovalent porous material (NPM) with a diamondoid crystal lattice. The permanent porosity in **12** and its unique gas sorption properties were verified by sorption of N₂, H₂, CO₂ and CH₄ at ambient and higher pressures as well as by grand canonical Monte Carlo (GCMC) simulations. The experimental and

simulated gas adsorption isotherms confirm the strong binding of H₂ to **12** cluster with a high heat of adsorption at zero coverage which can be rationalized in terms of occupation of the strong binding sites in the ultramicropockets on the surface of **12** involving discrete clusters in the first step of H₂ sorption. The significant H₂ capacity as well as the very high initial Q_{st} make **12** an interesting model system for discussing fundamental phenomena of H₂ adsorption in porous materials. The usefulness of the reported material is further exemplified by very high uptake for two gases that touch on environmental and energy aspects of carbon capture and methane storage. Again, gas sorption levels for CO₂ and CH₄ can be compared with the state-of-the-art MOFs and to our knowledge, the volumetric uptake for CH₄ is the highest reported for all NPMs. Finally, our studies underline the increasing potential of simple organozinc precursors featuring CO₂-reactive Zn-OH groups and proton-reactive Zn-C bonds for the design of new functional materials based on zinc carbonate components.

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