Reviewer's Report on the Ph. D. Thesis

Ing. Eva Káfuňková

PORPHYRIN-LAYERED DOUBLE HYDROXIDE HYBRIDS AS NOVEL PHOTOFUNCTIONAL MATERIALS

The Ph.D. thesis of Ing. Eva Káfuňková consists of a 55 page commentary based on six papers published in peer-reviewed journals that are attached in appendices. The work presented in the thesis is focused on the preparation and structural, spectroscopic, and photophysical characterization of layered double hydroxide systems intercalated with porphyrins and composites of these LDH with polymers. In a broader context, her work is directed to the area of hybrid functional materials. The motivation for studies of such compounds is their application in photogeneration of singlet oxygen as a bactericidal agent. This field at the borderline of inorganic, physical, and materials chemistry is currently a research area of exceptional activity.

The Introduction succinctly introduces a historical background and classification of hybrid materials, describes the structure, composition, properties, and applications of LDHs. Then it continues by discussing porphyrins and their properties, chemical design and synthesis of intercalates. Characteristics and methods of generation of singlet oxygen are also introduced. The chapter concludes with summary of characterization techniques useful for the study of LDH, their intercalated hybrid systems, and singlet oxygen generation. Hydroxyl ions should be hexagonally *close* packed (p. 8). Halocomplex should be $[NiCl_4]^{2-}$ and *heteropolyoxometallates* contain *molybdenum* $(PMo_{12}O_{40})^{3-}$ (p. 10). It would be better to add a legend to Fig. 6, the same as was used for Fig. 7. Quenching processes compete *successfully* with the phosphorescence (p. 19). Justification of the 2nd paragraph on p. 23 should be changed.

Results describe the preparation of MgAl LDHs with intercalated TPPS and PdTPPC. The synthetic procedures were probably not *adjusted* but modified or optimized on p. 29, 2nd line. Intercalation of porphyrins is evidenced by the XRD and TEM techniques. Thermal behavior was studied by HT-XRD and TG/DSC methods. Nearly perpendicular orientation of the porphyrin molecules to the LDH layers was deduced. UV/vis spectra ruled out aggregation of porphyrin molecules inside LDH. Time resolved diffuse reflectance measurements probed the decay of triplet state of porphyrins and luminiscence at 1270 nm was used to monitor the production of singlet oxygen and it lifetimes. Similarly, a related system of ZnAl LDH with an optimized Zn/Al ratio of 2 was also studied and it displays a better crystallinity. What decomposition is meant at the temperature of 310 °C for the Mg_2Al hybrid, TPPS? However, the ZnAl system proved to be ineffective in the singlet oxygen generation. Polymer composite films were prepared from porphyrin-intercalated LDH with polyurethane and polyester. Good dispersion was evidenced by the SAXS and TEM methods. Photosensitized production of singlet oxygen was observed and its lifetimes were measured.

I have the following questions concerning this work:

- It is stated on p. 30 that 100% porphyrin loading into LDH was not achieved. Is this a general situation for the LDH/porphyrin systems (known in the literature) and how it can be controlled/improved?
- It is known that the OH groups act as singlet oxygen quenchers. Why then dehydration of LDH decreases singlet oxygen production?

- What would be the difference between the porphyrin/LDH materials and porphyrin/silicagel systems (see e.g. Materials Research 6, 71-74, 2002) with respect to singlet oxygen production?
- What is the stability of the LDH/porphyrin/polymer films towards oxidative damage by singlet oxygen?
- Basal spacing for Zn_2Al-LDH with TPPS is 21.44 Å while Zn_2Al-LDH with Zn-TPPS increases to 22.95 Å. Does this increase correlate with the molecular sizes of TPPS and Zn-TPPS?
- What is the spacing of PdTPPS porphyrin molecules in the crystal lattice and how it compares with the values for its LDH intercalate?
- It is argued (CM 2007, 3828) from singlet oxygen decay kinetics in several solvents that oxygen senses different solvents upon exiting LDH. Is it possible that these differences are caused by effects of different solvent molecules diffusing into porphyrin/LDH?

The presented work of Ing. Eva Káfuňková is focused on a very topical area of materials based on LDH complexes with a large application potential. Synthetic experiments led to a number of new systems of MgAl and ZnAl LDH with controlled composition and their intercalates with selected porphyrin derivatives. Important results were obtained in the photogeneration of singlet oxygen form intercalates and their composite polymeric films. The author demonstrated her ability to carry out both synthetic experiments and a wide array of characterization measurements, such as XRD, IR, UV-vis, spectroscopic techniques, and thermal analysis. The author is also capable of analyzing obtained data and of drawing reasonable conclusion based on experimental facts. Color figures and graphs presented throughout the work clearly convey information to a reader. There is a negligibly small number of typos and errors in the thesis which were marked in the reviewer copy. The number (95) and the time-span of references show that the author possesses a good comprehension of the current status of the field and its recent development. Six published papers in reputable international journals describe the obtained research results. These peer-reviewed publications demonstrate Ing. Eva Káfuňková ability to summarize and clearly communicate her scientific findings. Furthermore she is the first author of two of these contributions.

In conclusion, I can declare that the overall amount and quality of this work is excellent for a doctoral thesis. I recommend this work to be **accepted** in partial fulfillment of requirements for a Ph. D. degree and graded A.

Brno, October 18, 2010

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