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# BOOK OF ABSTRACTS

# NEW HYBRID MATERIALS BASED ON NANOSTRUCTURED ALUMINUM OXYHYDROXIDE AND ANCHORED PORPHYRINS

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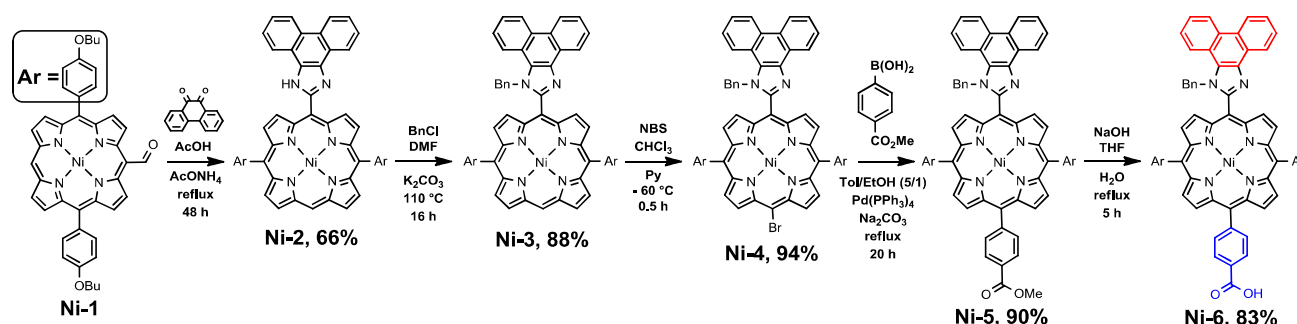
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The development of approaches towards new types of photoactive porphyrins is an actual field of the research. A challenging objective is to create a porphyrin-based hybrid material with catalytic properties. Nanostructured alumina oxyhydroxide (NAO) modified with a SiO<sub>2</sub> layer (NAOM) could be used as an inorganic component of the hybrid material. NAO is a highly porous material with fibril structure, which can be obtained by slow oxidation of an amalgam layer on the surface of aluminum plate. Its chemical formula can be written as Al<sub>2</sub>O<sub>3</sub>·nH<sub>2</sub>O, where n~3.6 [1]. Only one example of the immobilization of a tetrapyrrolic compound on the surface of NAOM is reported to the moment [2]. This work demonstrates a synthetic pathway for the preparation of non-symmetric porphyrins involving Radziszewski condensation (**Ni-2**) and subsequent C-C cross-coupling reaction using **Ni-4** (**Scheme 5**). The obtained porphyrin (**Ni-6**) contains anchoring group for further immobilization on the surface of NAOM as well as a polyaromatic fragment bridged *via* an imidazole moiety.



**Scheme 5.** Synthesis of the target bifunctional porphyrin.

It was found that direct bromination of **Ni-2** provided a mixture of compounds with relatively low yield, while the bromination of the benzyl-protected porphyrin (**Ni-3**) provided the target product in high yield. Moreover, the proton exchange process between the nitrogen atoms of the imidazole leads to significant broadening of signals in the NMR spectra, thus complicating their analysis. Benzylation of NH-fragment allows to avoid the exchange process so the spectra become interpretable.

An unexpected broadening of signals of the protons of *meso*-aryl groups in NMR spectra was found for all benzylated compounds. Most likely, the complexity of the obtained porphyrins results in a variety of dynamic processes. This phenomenon was studied by means of variable-temperature NMR. The decrease of temperature to 223K allowed the observation of all expected signals with fine resolution. Surprisingly, the complete inequivalence of all protons of *meso*-aryl groups was observed in **Ni-4 – Ni-6** NMR spectra.

Finally, complex **Ni-6** was immobilized on the surface of NAOM by treatment of the inorganic material with a DCM solution of the porphyrin. The grafting ratio of the obtained material was found to be 1 mg of porphyrin per 8 mg of NAOM. The quantitative evaluation was performed by the analysis of the residues after the immobilization by means of UV-vis spectroscopy. In turn, the obtained hybrid material was characterized by means of XPS, IR and UV-vis spectroscopy. The obtained stable hybrid material can be used in further research as a model of prospective photoactive materials.

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## References

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