



## Lehrstuhl Organische Chemie I

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## ОТЗЫВ

члена диссертационного совета на диссертацию Лукьянова Даниила Александровича на тему: «Синтез и исследование новых гетероциклических фотокатализаторов для превращения молекулярного кислорода в перекись водорода», представленную на соискание ученой степени кандидата химических наук по специальности 02.00.03 — Органическая химия

Hydrogen peroxide  $(H_2O_2)$  is an environmentally benign oxidant widely applied in the areas of organic synthesis, in particular oxidation reactions. The direct synthesis of  $H_2O_2$  by the metal-catalyzed reaction of molecular oxygen with hydrogen has recently proven to be feasible, but the high production cost and the unsatisfactory efficiency limited its practical application.

The motivation and desire to address some existing gaps prompted the research work summarized in the PhD thesis of Mr. Daniil Lukianov. In particular, the development of new heterocyclic molecular photocatalytic systems for the reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> became the focus of Mr. Lukianov's thesis. Mr. Lukianov contributions are specifically focused on the design and synthesis of photocatalysts and development of sophisticated methods for investigations of their potency in the reduction of different small molecules, among them O<sub>2</sub> and CO<sub>2</sub>. After giving an excellent introduction and state of the art literature overview in *Chapter 2*, Mr. Lukianov describes in *Chapters 3.1-3.4* his successful synthesis of corresponding starting compounds and planned porphyrin-derived dyads as well as oligomers via selected reactions. His subsequent *Chapters 3.4* and *3.5* describe the synthesis of fullerene derivatives and also porphyrin-fullerene dyads. His work resulted in wide variety of potential photocatalysts in good to high yields under reaction conditions used/optimized by Mr. Lukianov. Subsequently, Mr. Lukianov has succeeded in performing the selected photocatalyzed reactions (reduction of O<sub>2</sub>, CO<sub>2</sub>, nitrobenzene) using various photocatalysts and reaction conditions towards desired products (Chapter 3.6.1 – 3.6.4). Chapter 3 describe extensive, thoroughly executed pieces

of synthetic work and photocatalytic reactions. One also finds in Chapters 3 the successfully

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performed kinetic and reaction mechanism studies using complexes of transition metals (e.g., compound 11), as well as metal-free systems (e.g., compounds 108 and 118).

While nickel catalysts prepared by Mr. Daniil Lukianov did not exhibit photocatalytic activity in the selected model reactions, they could be used in future for photoelectrocatalysis. Mr. Lukianov established a research program that develops water-soluble cobalt porphyrinate, and also cobalt complexes supported on silica gel for generation of  $H_2O_2$  from  $O_2$ . Mr. Daniil Lukianov obtained new, interesting and useful results that he compiled in a comprehensive way in the submitted PhD thesis. The results are properly presented and discussed. I found the experimental section of his thesis to be also of high level, with all known and new compounds and new reactions fully documented. Of course, this is not really surprising, given that <u>4 publications</u> and <u>4 conference contributions</u> have already resulted from his work. This is very good productivity, particularly given the importance of his findings and kinetic studies, which he well summarized in his thesis and conclusions.

In summary, Mr. Lukianov is a productive young scientist who can carry out demanding organic syntheses of broad variety of compounds. Accordingly, I strongly support the acceptance of Mr. Lukianov's PhD thesis and recommend awarding Mr. Daniil Lukianov a PhD degree.

Диссертация Лукьянова Даниила Александровича на тему: «Синтез и исследование новых гетероциклических фотокатализаторов для превращения молекулярного кислорода в перекись водорода» соответствует основным требованиям, установленным Приказом от 01.09.2016 № 6821/1 «О порядке присуждения ученых степеней в Санкт-Петербургском государственном университете», соискатель Лукьянов Даниил Александрович заслуживает присуждения ученой степени кандидата химических наук по специальности 02.00.03 — Органическая химия.

Член диссертационного совета

Профессор органической химии в университете Эрлангена-Нюрнберга

Цогоева Светлана Батразовна 11.09.2019

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