

Oponentní posudek disertační práce

Ústav: Středoevropský technologický institut VUT

Akademický rok: **2024/2025**

Student (ka): **Ing. Lucie Kotásková**

Doktorský studijní program: **Pokročilé materiály a nanovědy**

Vedoucí disertační práce: **doc. Dr. Ing. Petr Neugebauer, Ph.D.**

Oponent disertační práce: **RNDr. Marek Cigáň, PhD.**

Název disertační práce: Syntéza molekulárních přepínačů funkcionalizovaných stabilními radikálovými substituenty

Aktuálnost tématu disertační práce:

The core topics of the submitted dissertation thesis are organized into two primary themes: (1) halogen-substituted diarylhydrazone photoswitches and (2) stable radical-substituted diarylhydrazone photoswitches. The dissertation primarily focuses on externally stimuli-responsive molecules that exhibit reversible changes in their physicochemical properties — an area that represents a current trend in modern physical organic and materials chemistry.

Splnění stanovených cílů:

The objectives set out in the dissertation have been achieved.

Postup řešení problému a výsledky disertace:

The author employed standard procedures of organic synthesis and characterization of the prepared compounds, as well as appropriate techniques and methods for evaluating the fundamental parameters of the synthesized hydrazone photoswitches.

The presented research has led to the preparation of two manuscripts submitted to reputable Q2 JCR journals — one already published in *RSC Advances* and another currently under review in *ACS Organic & Inorganic Au*. Additionally, a third manuscript is in preparation. Lucie is listed as the first author on all three. She is also a co-author of a previously published article from her PhD work in *Crystal Growth & Design* (Q1 JCR), which explores the modulation of spin-transition temperatures in an iron(III) complex through variations in crystallization solvent composition. This publication record clearly reflects the good quality and scientific merit of the dissertation.

Význam pro praxi nebo rozvoj vědního oboru:

The results obtained contribute to the advancement of physical organic chemistry and materials chemistry in the field of novel molecular photoswitches.

Formální úprava disertační práce a její jazyková úroveň:

The thesis spans 159 pages, excluding the Appendix, and is structured into 11 chapters, including sections such as Conclusions and Perspectives, Author's Publications and Outputs, References, and the Appendix. The dissertation meets a high formal standard, demonstrating very good English and precise use of professional terminology. It is virtually free from formal mistakes, and the figures and schemes are of high graphic quality. The work is well-structured, with logically organized chapters that progress clearly and cohesively.

(Small) Comments:

- Pages 15 and 74: N-oxoammonium salt and β -ketoesters should be written with letters N and β in italic as "N-oxoammonium" and " β -ketoesters", respectively.

Zda disertační práce splňuje podmínky uvedené v § 47 odst. 4 zákona:

(4) Studium se řádně ukončuje státní doktorskou zkouškou a obhajobou disertační práce, kterými se prokazuje schopnost a připravenost k samostatné činnosti v oblasti výzkumu nebo vývoje nebo k samostatné teoretické a tvůrčí umělecké činnosti. Disertační práce musí obsahovat původní a uveřejněné výsledky nebo výsledky přijaté k uveřejnění. 1)

The dissertation meets the requirements set out in Section 47, Subsection 4 of the Higher Education Act.

Připomínky a dotazy:

General comments to the research:

Better care should be taken when describing proton NMR spectra. In many cases, there are several errors. For example, the ^1H NMR of compound **10b** on page 101 is given:

Yellow powder, 74%. ^1H NMR (700 MHz, CDCl_3): d 14.88 (s, 1H, N-H), 8.67 (d, J = 4.8 Hz, 1H), 8.23 (d, J = 8.3 Hz, 1H), **7.97 (t, J = 1.8 Hz, 1H)**, **7.83 (td, J = 15.8, 1.6 Hz, 1H)**, 7.77–7.71 (m, 2H), 7.46 (t, J = 7.8 Hz, 1H), 7.30 (dd, J = 12.4, 7.4, 4.9, 2.5 Hz, 1H), 4.42 (q, J = 7.1 Hz, 2H), 1.46 (t, J = 7.1 Hz, 3H).

Interaction constants in the aromatic region do not have such values (around 15 Hz), and no triplets or quadruplets are present in this region either. These types of errors are found throughout the document. On the other hand, I value the structural characterization of the synthesized compounds through X-ray crystallography. Further, a general graphical abstract at the beginning of the document could be useful for the reader, and I would also welcome a short chapter devoted to triarylhydrazone photoswitches.

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¹ § 10 zákona č. 35/1965 Sb., o dílech literárních, vědeckých a uměleckých (autorský zákon).



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Discussion questions:

- 1) From my point of view, the role of hydrazone photoswitching unit in design of paramagnetic probes/adaptive agents for diagnostics/therapeutics or supramolecular chemistry is not clearly described in the thesis. Can you explain a general design strategy?
- 2) Please, explain why is the ketone part of hydrazone molecules in the thesis called "rotor" part of the photoswitch?
- 3) Most of the pyridine rotor-based diarylhydrazone photoswitches in the thesis exhibit poor photoswitching due to photochemically locked isomer by intramolecular hydrogen bonding (the highest photoconversion was 49%). Moreover, the significant overlap of the isomers' spectra results in the poor addressability of the photoswitch and thus further supports the limited switching. Why did you select this skeleton for your research? Can you describe the competitive pathways to photoisomerization of hydrazone photoswitches with intramolecular hydrogen bonding?
- 4) Photoswitching efficiency:
Although you did not quantify the photochemical efficiency (photoisomerization quantum yields) of your photoswitches, you suggested its calculation from simple mono-exponential fit of an absorbance decrease during irradiation (Eq. 15; page 46). I think that such simplification could lead to a significant overestimation of the corresponding QY in the case of your photoswitches. Can you explain why?
- 5) Photoswitching mechanism for molecules **8** and **9** (pages 93-96):
 - a) Photoisomerization of both di- and triaryl-hydrazone photoswitches described in the literature (*J. Phys. Chem. A* 2020, 124, 6411; *J. Org. Chem.* 2021, 86, 17, 11633; *Chem. Eur. J.* 2024, 30, e202303509) happens on the singlet energy surface of the excited isomer. Contrary to this conclusion, your photoisomerisation process starts from proton transferred tautomer (Z-pyH, Figure 41) which is 5-6 kcal/mol higher in energy compared to the initial Z isomer and thus cannot be populated in the solvent. Why doesn't the initial Z isomer relax by N=N rotation on the S₁ energy hypersurface (form molecule **9** on the doublet hypersurface)?
 - b) What drives the intersystem crossing to the triplet T₁ state of the excited molecule? How could you confirm and possibly quantify the efficiency of the transition to the triplet state? Did you calculate the spin-orbit coupling (SOC) constant?

Celkové zhodnocení disertační práce:

Overall, the work clearly meets the requirements for a dissertation thesis. After a successful defence, I propose to award the author the academic title of "philosophiae doctor" ("PhD.") and a classification level „PROSPELa“ from the subject „Defence of the Dissertation Thesis“ in the sense of Section 47(4) of Act No. 111/1998 Coll., on Higher Education Institutions.

Disertační práci Ing. Lucie Kotáskové doporučuji/~~nedoporučuji~~ k obhajobě pro udělení akademického titulu "doktor" (Ph.D.).

V. BEATTISIAVE dne 16. 05. 2025

RNDr. Marek Cigáň, PhD.