1. PHD PROJECT DESCRIPTION (4000 characters max., including the aims and work plan)

Project title: Photochromic organic solar cells based on azo dyes

1.1. Project goals

The goal of this project is to design and investigate novel photoswitchable molecules for photovoltaic applications. Particularly, the work will focus on using azobenzene-type materials to improve the efficiency of organic solar cells (OSCs). Since the intramolecular charge transfer is a vital feature employed in the design of new optical materials, the azo molecules undoubtedly outperform many basic heterocyclic scaffolds not frequently used in organic solar systems. Therefore, such molecules can be added to the active layer of solar cells, improving the efficiency of the device. In order to further increase the efficiency of solar cells composed of selected azo dyes, the goal is to fabricate nanoscale-patterned active layer to increase optical path length in such layer due to scattering of illuminating light. A comprehensive study of new families of molecular architectures will be carried out to better understand the mechanisms of photoactivation and the possibility of exploiting their photovoltaic properties. Knowledge of these parameters is necessary for the use of these compounds in OSCs.

1.2. Outline

Azo dyes possess unique photophysical and photochemical properties. In particular, their photoisomerization between *trans* and *cis* forms due to absorption in the UV-Vis region makes them promising candidates for applications in photovoltaics. Azo dye-based solar cells are cheap, environmentally friendly, and have a higher molecular extinction coefficient than other solar cells. By modifying the substituents in the azobenzene core, it is possible to tailor their HOMO/LUMO energy levels, which makes them flexible in tuning the energy alignment with electron donors or acceptors in OSCs. The *trans-cis* photoisomerization also leads to photoinduced mass transport that stands behind surface relief grating (SRG) formation upon light irradiation. Such a process is a low-cost way for obtaining nanoscale patterning in the solar cell layer, which helps to trap the light due to its scattering and thus increases optical path length and improves light absorption. This is particularly useful in the case of low-efficiency solar cells that struggle with energy conversion. *Trans-cis* isomerization can also be used to modulate the properties of the active layer, enabling light-controlled or switchable solar cells. Therefore, azo dyes can be used as sensitizers to broaden the absorption spectrum and improve light collection. Therefore, the ability to fabricate SRG, combined with azobenzene's light absorption properties, facilitates the improvement of photovoltaic cell efficiency. The proposed project will be a significant program of fundamental research on effects related to engineered novel azo dye materials. The obtained results will pave the way for the use of azo-dye materials in photovoltaic technology on a much wider scale than it has been done so far.

1.3. Work plan

Several experimental techniques will be used to study optical and photovoltaic properties of proposed azo-dye materials as well as the usefulness of such materials for photovoltaics. Particularly, the dynamics of material modification under the light stimuli will be studied with the two-beam technique. In this experiment, two overlapping laser beams interfere on the surface of the material, forcing it to react, which is observed as surface-relief grating formation. For the most perspective azo dyes, simple solar cells will be made. Current-voltage measurements will be performed for the prepared OSC structures.

1.4. Literature *(max. 7 listed, as a suggestion for a PhD candidate preliminary study)*

[1] S.-I. Na, S.-S. Kim, S.-S. Kwon, J. Jo, J.n Kim, T. Lee, D.-Y. Kim, Surface relief gratings on poly„3-hexylthiophene and fullerene blends for efficient organic solar cells, *Appl. Phys. Lett. 91, 173509 (2007) DOI: 10.1063/1.2802561*

[2] S.-I. Na, S.-S. Kim, J. Jo, S.-H. Oh, J. Kim, D.-Y. Kim, Efficient Polymer Solar Cells with Surface Relief Gratings Fabricated by Simple Soft Lithography, *Adv. Funct. Mater.18, 3956–3963 (2008) DOI: 10.1002/adfm.200800683*

[3] L. Müller-Meskamp, Y.H. Kim, T. Roch, S. Hofmann, R. Scholz, S. Eckardt, K. Leo, A.F. Lasagni, Efficiency Enhancement of Organic Solar Cells by Fabricating Periodic Surface Textures using Direct Laser Interference Patterning, *Adv. Mater. 24, 906–910, (2012) DOI: 10.1002/adma.201104331*

[4] K. Li, H. Zhen, Z. Huang, G. Li, X. Liu, Embedded Surface Relief Gratings by a Simple Method to Improve Absorption and Electrical Properties of Polymer Solar Cells, *ACS Appl. Mater. Interfaces 4, 4393−4397 (2012) DOI: 10.1021/am301059j*

[5] G. Tadeson, R.G. Sabat, Enhancement of the Power Conversion Efficiency of Organic Solar Cells by Surface Patterning of Azobenzene Thin Films, *ACS Omega 4, 21862−21872 (2019) DOI: 10.1021/acsomega.9b02844*

[6] B. Derkowska-Zielinska, E. Gondek, M. Pokladko-Kowar, A. Kaczmarek-Kedziera, A. Kysil, G. Lakshminarayana, O. Krupka, Photovoltaic cells with various azo dyes as components of the active layer, *Solar Energy 203, 19 (2020) DOI: 10.1016/j.solener.2020.04.022*

[7] B. Derkowska-Zielinska, D. Szmigiel, A. Kysil, O. Krupka, A. Kozanecka-Szmigiel, Photoresponsive behavior of heterocyclic azo polymers with various functional groups, *Journal of Physical Chemistry C 124, 939-944 (2020) DOI: 10.1021/acs.jpcc.9b10495*

1.5. Required initial knowledge and skills of the PhD candidate

Master's in Physics or Master's in Chemistry or related fields of Natural Sciences. Basic physics, basic organic chemistry and spectroscopy, basic experience in experimental optics, communicative English written and spoken, programming skills highly appreciated, ability to work both independently and in a team, eagerness to take on challenges, and motivation to conduct scientific research.

1.6. Expected development of the PhD candidate's knowledge and skills

The project is aimed at optimizing azo-materials responsive to light activation suitable for organic solar cells. The candidate will gain comprehensive skills in spectroscopic measurements by using several experimental techniques (which involve necessary theory, building/modifying the experimental setups, and collecting data from the experiments). In addition, the crucial part of the research will be to analyze, interpret, and present the results during meetings, seminars, and conferences. Therefore, the project will provide a PhD candidate with an exceptionally strong and complete background for the rational design of organic optical materials from scratch as well as the development of knowledge and skills in the field of photovoltaics and nonlinear optics. Additionally, a PhD student will learn the basics of programming and data analysis.