Introduction

The goal of the proposed research, in a broader perspective, was the development of a research program centering on photochromic molecular switches with special attention to their integration into more complex (in)organic environments. During the project years we developed the synthetic expertise and the characterization workflow of such molecules and established the necessary collaborations for the characterization of interfacial systems. The summary of the obtained results and encountered difficulties are detailed below.

Results on catalytic particles/switchable catalysis

Our initial vision on the development of photoswitchable heterogeneous cooperative catalysis could not be realized, although several approaches were tested. The original idea that was based on the proximity of surface-confined acidic and basic functional groups, where the basic unit was part of a photoswitchable azobenzene molecule, turned out not to be feasible due to the inaccessible structure of the photoswitchable base. The benzylamine type structure on one end of the azobenzene was incompatible with the transition metal catalyzed introduction of the surface-binding silane group on the other end of the photochrome. The amine unit turned out to be a catalyst poison. Several synthesis redesigns were attempted, however none of them provided the required substitution pattern.

As a complementary strategy, we also attempted a supramolecular approach to light-controlled cooperative acid-base catalysis. In this attempt we experimented with systems where either the acid or the base was grafted to a solid surface, while the other component was present in solutions. The expectation was that the two components would be in an acid-base interaction, hence, in the proximity of each other that is key for the activation of the reactants of a reaction. We also envisioned that this interaction could be manipulated by light, through changing the structure of the isomerizable unit. Unfortunately, none of these systems provided enhanced activity in the model cyanation reaction.

Nevertheless, due to our strong interest in photoswitchable catalysis, we changed plans and focused on a different approach to photoswitchable heterogeneous catalysis. We aimed at photoswitchable solubility control, which could turn a solid (poorly soluble) catalyst into a soluble one that, in turn, would lead to enhanced catalytic activity (Figure 1).

We designed and synthesized a click-derived Pd-complex merged with a photoswitchable azobenzene unit. While in the *trans*-form of the switch the complex showed limited solubility, the photogenerated *cis*-form rendered the molecule soluble in polar solvents. This light-controllable solubility was exploited to affect the catalytic activity in the Suzuki coupling reaction. The effect of the substrate and catalyst concentration and light intensity on the proceeding and outcome of the reaction was studied. Dehalogenation of the aryl iodide starting material was found to be a major side reaction; however, its occurrence was dependent on the applied light intensity.

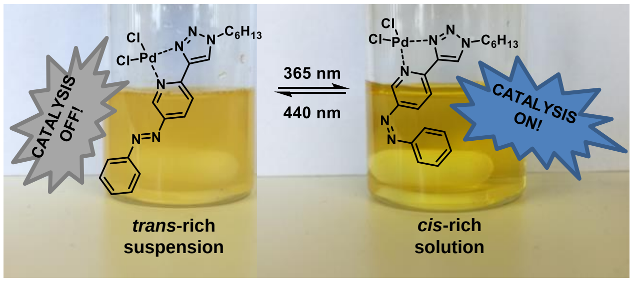

Figure 1. Light-controlled catalytic activity in Suzuki coupling reaction by a Pd-complex with photoswitchable solubility.

Research output related to catalytic particles/switchable catalysis

Publications

- Tamás Gazdag, Attila Kunfi, Gábor London*
  Cyanation of aryl bromides with $K_4[Fe(CN)_6]$ using polydopamine supported Pd nanoparticle catalysis: formation of magnetite during the reaction.
  React. Kinet. Mech. Catal. **2018**, *125*, 567-581.

- Attila Kunfi, Gábor London*
  Polydopamine: An Emerging Material in the Catalysis of Organic Transformations.
  Synthesis **2019**, *51*, 2829 – 2838.

- Attila Kunfi, István Jablonkai*, Tamás Gazdag, Péter J. Mayer, Péter Pál Kalapos, Krisztina Németh, Tamás Holczbauer, Gábor London*
  A photoresponsive palladium complex of an azopyridyl-triazole ligand: light-controlled solubility drives catalytic activity in the Suzuki coupling reaction
  RSC Advances **2021**, *11*, 23419-23429.

- István Jablonkai, Attila Kunfi, Da-Hui Qu, Gábor London*
  A new color in green chemistry: Photochromic molecular switches as components of multifunctional catalytic systems
  In: Török, B; Schäfer, C (Eds.) Non-Traditional Activation Methods in Green and Sustainable Applications: Microwaves; Ultrasounds; Photo-, Electro- and Mechanochemistry and High Hydrostatic Pressure Amsterdam, The Netherlands: Elsevier Inc. **2021**, 241-28

Conference presentations

- London Gábor
  Változatok palládium-katalízisre (szóbeli előadás)
  Katalízis Munkabizottság ülése, Budapest, **2021**. 12. 13.

- Jablonkai István, Gazdag Tamás, Mayer Péter, Kalapos Péter, London Gábor
  Egy fotokapcsolható palládiumkomplex aktivitásának vizsgálata Suzuki reakciókban (szóbeli előadás)
  Heterociklusos és Elemorganikus Munkabizottság ülése, Balatonszemes, **2022**. május 23-25.

- István Jablonkai, Attila Kunfi, Tamás Gazdag, Péter József Mayer, Péter Pál Kalapos, Gábor London
  Photoresponsive palladium complexes with azopyridyl-triazole ligands. Light-controlled solubility affects catalytic activity in Suzuki-coupling reaction (Poster presentation)
  19th International Symposium on Novel Aromatics, Warsaw, **2022**. July 3–8.

Thesis

- Ádám Baróthi: "Fotokémiailag aktivált heterogén kooperatív katalízis bázikus azobenzolokkal" (*MSc Thesis*, Eötvös Loránd Tudományegyetem, Természettudományi Kar, Kémiai Intézet, **2018**)

Results on polydopamine (PDA)/ molecular switch conjugates

We have shown that a PDA/Au composite material provides an easily assembled surface for azobenzene photoisomerization (Figure 2). Fast and reversible photo-switching of azobenzenes on the Q-PDA-Au surface was not affected by the surface binding group (-NH_2, -SH) and the spacer length (C_3, C_6) of the azobenzene molecules under the measurement conditions. As the gold component of Q-PDA-Au was present in the form of Au particles, their curved surface facilitated ligand exchange, which was exploited to construct a multicomponent photoswitchable dynamic interface by using a red-shifted azobenzene as exchanging ligand. Dynamic interfaces that can be addressed with orthogonal wavelengths could be applied in the construction of surface polarity gradients or suitable to control multiple interactions between a single surface and different analytes with independent external stimuli. Given the universal adherent nature of PDA, such photoswitchable surfaces can be prepared on virtually any material.

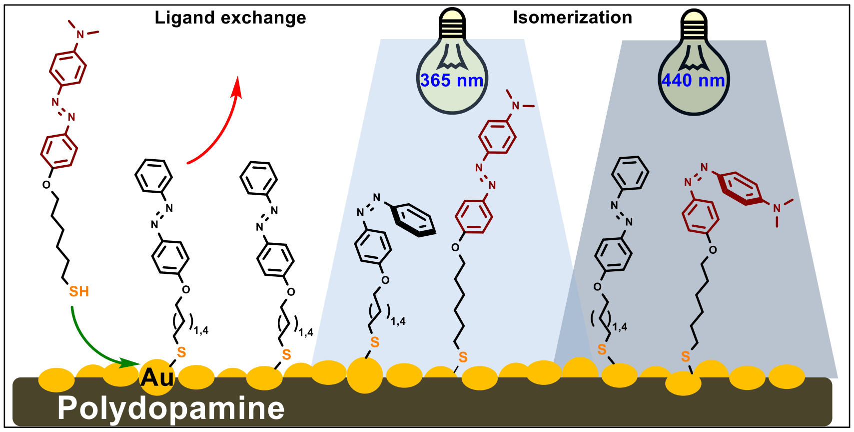

Figure 2. Photoswitchable macroscopic solid surfaces based on azobenzene-functionalized polydopamine/gold nanoparticle composite materials.

We constructed a donor−acceptor Stenhouse adduct molecular layer on a gold surface (Figure 3). To avoid the incompatibility of the thiol surface-binding group with the donor−acceptor polyene structure of the switch, an interfacial reaction approach was followed. Poly(dopamine)-supported gold nanoparticles on quartz slides were chosen as substrates, which was expected to facilitate both the interfacial reaction and the switching process by providing favorable steric conditions due to the curved particle surface. The reaction between the surface-bound donor half and the CF_3-isoxazolone-based acceptor half was proved to be successful by X-ray photoelectron spectroscopy (XPS). However, UV−vis measurements suggested that a closed, cyclopentenone-containing structure of the switch formed on the surface irreversibly. Analysis of the wetting behavior of the surface revealed spontaneous water spreading that could be associated with conformational changes of the closed isomer.

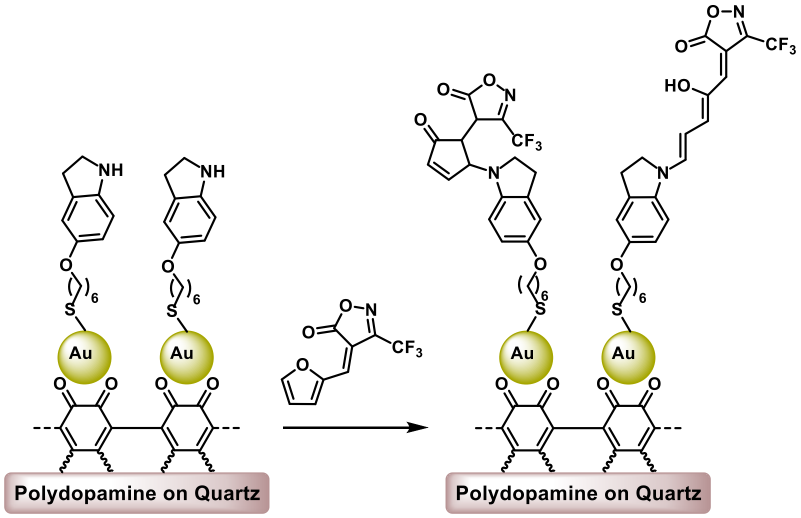

Figure 3. Donor–acceptor Stenhouse adducts on gold surfaces.

We have studied the light-induced and thermal properties of azobenzenes on morphologically different PDA-Au substrates (Figure 4). Gold particulate systems were prepared on polydopamine coated surfaces, where the catecholic units of the polymer acted as a reducing agent. Different surface morphologies were obtained by using different Au(III) reduction times. Shorter immersion of the PDA-modified surfaces into an aqueous Au(III) solution led to lower level of aggregation, while longer immersion times led to gold particle covered surfaces. Too long reduction time (48 h), however, led to the loss of PDA-Au layer from the supporting quartz substrate. The morphology of the nanoparticulate surfaces obtained after 1 h and 24 h immersion times were characterized by AFM and KPFM techniques. Azobenzene derivatives having different chain-lengths equipped with a terminal thiol binding group were successfully attached to the prepared surfaces as detected by UV-Vis and wettability measurements. Regarding their photochemical properties on the surface, each molecule exhibited fast and reversible photoswitching, comparable to what was observed in solution. The extent of photoisomerization was found somewhat lower in the case of shorter spacer length that could be due to partial quenching by the proximal gold surface. The largest impact of the nanoparticulate system was on the thermal cis-to-trans isomerization of the attached molecules. This process was found to be faster on the surface compared to solution, which is the first demonstration of enhanced thermal azobenzene isomerization in a solvent-free, metal particle-based condensed phase.

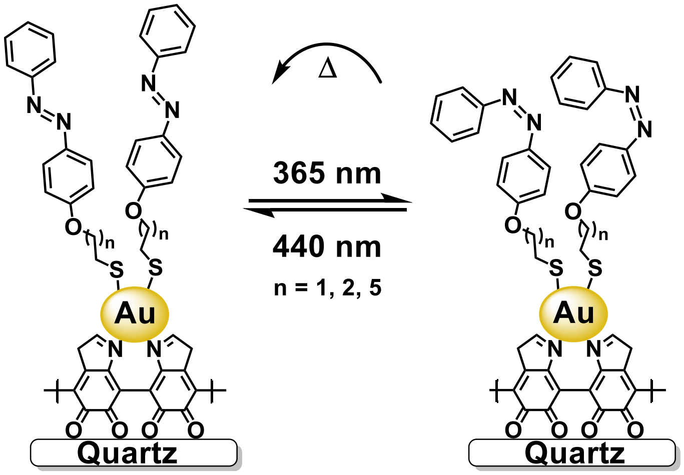

Figure 4. Light-induced and thermal isomerization of azobenzenes on immobilized gold nanoparticle aggregates.

Research output related to polydopamine (PDA)/ molecular switch conjugates

Publications

- Attila Kunfi, Rita Bernadett Vlocskó, Zsófia Keresztes, Miklós Mohai, Imre Bertóti, Ágnes Ábrahám, Éva Kiss; Gabor London*
  Photoswitchable Macroscopic Solid Surfaces Based On Azobenzene-Functionalized Polydopamine/Gold Nanoparticle Composite Materials: Formation, Isomerization and Ligand Exchange
  ChemPlusChem **2020**, *85*, 797-805.
  (*Highlights*: The paper was highlighted as „Cover Feature" by the journal, it was included in the "Hot Topic: Gold" collection of the publisher and was highlighted by ChemistryViews Magazine:
  https://www.chemistryviews.org/details/ezine/11227443/Gold_Nanoparticle_Arrays_on_Surfaces.html)

- Dalma Edit Nánási, Attila Kunfi, Ágnes Ábrahám, Péter J. Mayer, Judith Mihály, Gergely F. Samu, Éva Kiss, Miklós Mohai, Gábor London*
  Construction and Properties of Donor–Acceptor Stenhouse Adducts on Gold Surfaces
  Langmuir **2021**, *37*, 3057-3066.

- Attila Kunfi, Ágnes Ábrahám, Gergő Gyulai, Éva Kiss, Gabor London*
  Light-Induced and Thermal Isomerization of Azobenzenes on Immobilized Gold Nanoparticle Aggregates
  ChemPlusChem **2022**, *87*, e202200153.

Conference presentations

- Attila Kunfi, Rita Bernadett Vlocskó, Gábor London
  Construction of heterogeneous catalysts and dynamic interfaces on a polydopamine platform (Poster presentation)
  European Symposium on Organic Chemistry, Vienna, Austria, **2019**. July 14–19.

- Attila Kunfi, Rita Bernadett Vlocskó, Gábor London
  Application of polydopamine in the construction of efficient heterogeneous catalysts and dynamic interfaces (Poster presentation)
  International Conference on Adhesion in Aqueous Media: From Biology to Synthetic Materials, Dresden, Germany **2019**. September 9–13.

- Attila Kunfi, Dalma Edit Nánási, Ágnes Ábrahám, Éva Kiss, Miklós Mohai, Gábor London Photoswitches on gold nanoparticle-doped macroscopic solid surfaces (Poster presentation) *19th International Symposium on Novel Aromatics,* Warsaw, **2022**. July 3–8.

Theses

- Rita Bernadett Vlocskó: "Dinamikusan kontrollálható, fotoaktív azobenzolokat tartalmazó határfelületi rendszerek" (*MSc Thesis*, Budapesti Műszaki és Gazdaságtudományi Egyetem, Vegyészmérnöki és Biomérnöki Kar, **2019**.)

- Dalma Edit Nánási: "Fotoizomerizálható donor-akceptor Stenhouse-adduktok szintézise és felülethez kapcsolása határfelületi reakcióval" (*BSc Thesis*, Eötvös Loránd Tudományegyetem, Természettudományi Kar, Kémiai Intézet, **2019**.)

- Attila Kunfi: „Polidopamin alkalmazása a szerves kémiában: katalizátor hordozótól a fotoizomerizálható felületekig" (*PhD Thesis*, Szegedi Tudományegyetem Természettudományi és Informatikai Kar, Kémia Doktori Iskola, **2020**.)

Results on the development of novel molecular switches

We have synthesized dithienylbenzene and reported ^{1}H NMR evidence that this compound undergoes electrocyclization upon irradiation with UV-light of 254 nm (Figure 5). Furthermore, through a detailed computational analysis, we have found that the electrocyclization process is facilitated by photoinduced changes in the aromaticity of the benzene motif of the molecule. More specifically, there is a loss of aromaticity during the initial photoexcitation that produces a reactive, antiaromatic excited state, and subsequently a relief of this antiaromaticity. Altogether, the results of this work show that the concept of excited state aromaticity holds substantial promise as a tool for designing potent electrocyclization-based photoswitches within the framework of dithienylethenes.

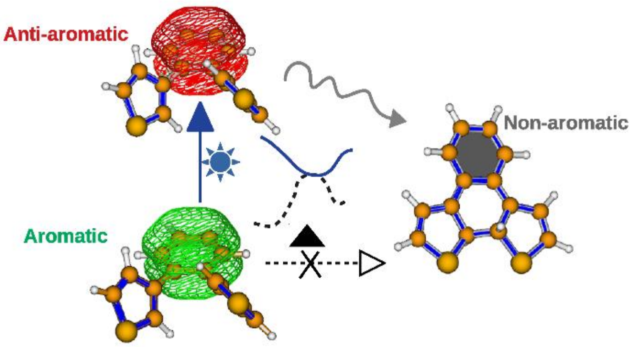

Figure 5. Photoinduced changes in aromaticity facilitate electrocyclization of dithienylbenzene switches.

We have demonstrated efficient and reversible photoswitching by diarylethenes featuring a biphenylene group as the ethene bridge between the two aryl units (Figure 6). Starting with a compound for which thienyl groups constitute the aryl core, the photoswitching is assessed experimentally using UV-Vis and NMR spectroscopies. Probing changes in the local (anti)aromaticity of the individual rings of the biphenylene in terms of experimental ^{1}H NMR chemical shifts and calculated NICS, HOMA and SA aromaticity indices, it is found that the character of each ring is altered through the photoswitching. Although this molecule is found to undergo reversible photoswitching, the process is hampered by the irreversible formation of an annulated bis(dihydro-thiopyran) side-product. Next, to bypass this problem and improve the fatigue resistance of the switch, which is a prerequisite for its potential use in applications, the thienyl groups in the aryl core were replaced by thiazolyl groups. This structural change resulted in a switch capable of reversible operation under ambient conditions without considerable degradation even after multiple switching cycles. Overall, we conclude that the photoswitching can be used to control the local (anti)aromatic character of each ring of the biphenylene in a reversible fashion.

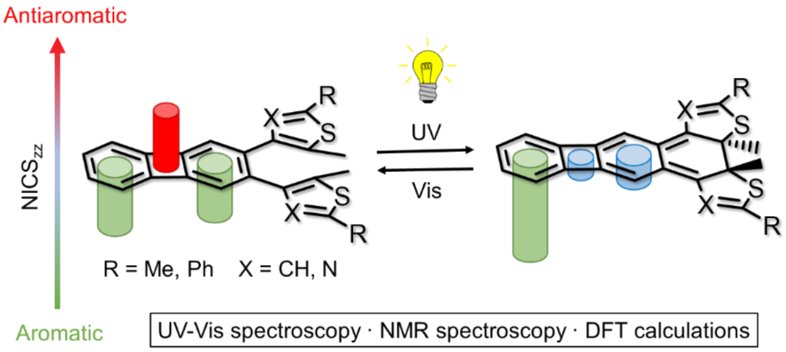

Figure 6. Photoswitching of local (anti)aromaticity in biphenylene-based diarylethene molecular switches.

Research output related to the development of novel molecular switches

Publications

- Baswanth Oruganti,* Péter Pál Kalapos, Varada Bhargav, Gábor London,* Bo Durbeej* Photoinduced Changes in Aromaticity Facilitate Electrocyclization of Dithienylbenzene Switches
  J. Am. Chem. Soc. **2020**, *142*, 13941−13953.

- Péter Pál Kalapos, Péter J. Mayer, Tamás Gazdag, Attila Demeter, Baswanth Oruganti*, Bo Durbeej*, Gábor London*
  Photoswitching of Local (Anti)Aromaticity in Biphenylene-Based Diarylethene Molecular Switches
  J. Org. Chem. **2022**, Accepted (https://doi.org/10.1021/acs.joc.2c00504)

Conference presentation

- <u>Péter P. Kalapos</u>, Péter J. Mayer, Tamás Gazdag, Baswanth Oruganti, Bo Durbeej Gábor London
  Photoswitching of local ground-state aromaticity in polyciclic polycyclic conjugated systems (Poster presentation)
  19th International Symposium on Novel Aromatics, Warsaw, **2022**. July 3–8.

Thesis

- Péter Pál Kalapos: Photochromic switching of a [4n] π electron system (*MSc Thesis*, ELTE Kémiai Intézet, **2022**)