

Abstract

Photocatalysis, the process of converting light energy into chemical energy, might be a key way of addressing challenges with global energy and fuel availability. One of the most promising direction of research might be using photocatalysis for water splitting to produce hydrogen. Developing efficient, stable, and cost-effective organic photocatalysts is vital for achieving true environment-friendly way of producing this important fuel.

The aim of this work was screening of novel, perylene diimide (PDI) and benzothiadiazole (BTDZ) based organic compounds for use as photocatalysts and photosensitizers in the hydrogen evolution reaction (HER). My work involved designing PDI and BTDZ derivatives together with density functional theory (DFT) calculations, synthesis and confirmation of the identity of obtained compounds. Obtained compounds were tested for photocatalytic activity.

Main strategies employed in the design of target compounds were: obtaining structures containing donor-acceptor (D-A) motif to facilitate charge separation, incorporating anchoring groups for effective attachment to TiO₂|Pt nanoparticles, and utilizing the heavy-atom effect to enhance intersystem crossing (ISC) and prolong the lifetime of catalytically active excited states.

In my research, I first synthesized a series of bay-substituted PDI derivatives with a D-A motif (**A-series**) via palladium-catalyzed Suzuki coupling. Subsequently, I developed a selective, two-step procedure to synthesize PDI derivatives containing a single carboxylic acid anchoring group (**B-series**), which involved a Sonogashira coupling followed by a Suzuki coupling. For comparison purposes, I also synthesized a model compound (**M5**), which is a perylenomonoimide (PMI) derivative. To investigate the heavy-atom effect, I synthesized halogenated derivatives of the most promising compounds via halogenation reaction with N-halosuccinimides. To monitor progression of the halogenation, I optimized conditions for analysis of these compounds on HPLC. The BTDZ derivatives (**C-series**) were synthesized via Suzuki coupling, where I

optimized reaction conditions by changing ligand and employing crown ether to prepare BTDZ derivatives with amino or carboxylic anchoring groups. I confirmed the structures of all obtained compounds using MALDI-TOF MS and ^1H NMR before evaluating their photocatalytic activity.

A key achievement was isolation and confirmation of the structure of the species derived from carbazole-substituted PDI (**A4**) formed during photoirradiation in the presence of platinum salts. This ring-opened PDI-platinum complex, formed *in situ* during photoirradiation, was proven to be a part of highly active molecular catalyst with a core-shell structure.

The PDI derivatives with an anchoring group (**B-series**) successfully photosensitized a $\text{TiO}_2|\text{Pt}$ system, where the brominated carbazole derivative (**B12**) showed the highest activity, proving the positive impact of the heavy-atom effect. What is very important, these halogenated derivatives functioned without a sacrificial electron donor, confirming enhanced charge separation in the PDI derivatives with heavy atom modified donors.

Finally, the BTDZ derivatives were tested in a completely metal-free system, where they successfully photosensitized graphene quantum dots (GQDs) for HER. In these tests **C3** showed outstanding performance. This confirmed the fact that the synthesized compounds are able to act as photosensitizers for HER in fully organic photocatalytic systems.