There has been recent interest in using biopolymers as templates to construct photonic structures and devices. Unquestionably, the most important biopolymer for such an application is DNA, which represents an astonishing nano-scale scaffold for assembly of light-responsive moieties with potential application in fields like biological, physical and material sciences. Among various canonical and noncanonical DNA structures G-quadruplexes (G4es), four-stranded motifs consisting of cores of π-π stacked G-quartets stabilized by Hoogsteen hydrogen bonds and centrally coordinated metal ions, e.g. Na^{+}, Mg^{2+}, K^{+}, have attracted particular attention. This stems from the fact that they are involved in key cellular events especially those which are disease- and aging-related. However, these structures are also attractive to build DNA-based nanoarchitectures, their capability to form higher order structures provides an excellent module to be used in the design of nanodevices. The key to achieving practical applications of such DNA-based nanosystems is to control the operations of them by external stimulus. Light is the most desired kind of stimulus, because spatiotemporal resolution, excitation tunability or biocompatibility is achieved through remote control. A particularly important group of compounds in this case are azobenzenes, well known photochromic switches. Their relatively easy synthesis and the possibility of modification make these compounds widely used in various applications. Azobenzene derivatives can occur in either *cis* (*Z*) or *trans* (*E*) conformation, however at equilibrium in the dark, this moiety exists as the more stable *trans* isomer. Irradiation with light of proper wavelength induces a molecular geometry change leading to the *cis* isomer, which can revert back to the *trans* state thermally or upon irradiation (Fig.1). Due to the fact that these isomers have different geometries, their properties differ significantly, the *trans* isomer is almost flat and has no dipole moment, whereas the *cis* form presents an angular geometry and a dipole moment of 3.0 D. This features makes azobenzene an excellent photoresponsive molecular tool to create smart hybrid DNA-based nanostructures.

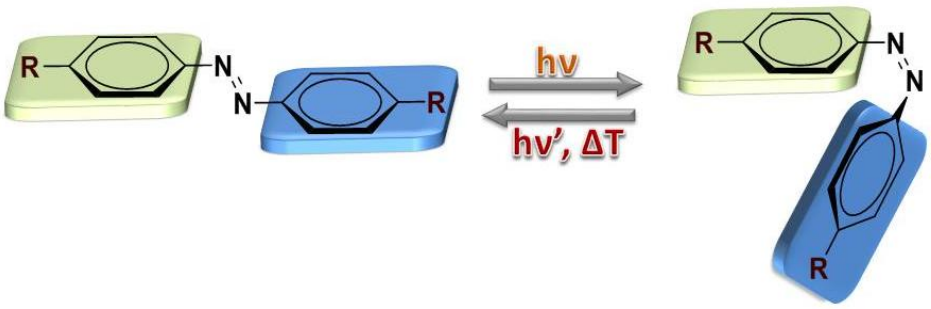

Figure 1. Isomerization pathway of azobenzene.

A major chiral motif present in the nature is helicity, found at macro- and supramolecular level in numerous structures of biomolecules like proteins or nucleic acids. This natural chirogenic environment provides opportunities for developing complex hybrid systems with enhanced optical properties due to the fact that chiral compounds exhibit rigorous selectivity of binding toward inherently chiral DNA matrices. In this context, incorporation of chiral azobenzene derivatives into a chiral biopolymer may lead to groundbreaking smart chiroptical responsive systems with a dramatically improved spatiotemporal control.

This project proposes synthesis of new, water-soluble, chiral molecular probes based on the azobenzene motif. These bistable, chiral stimuli-responsive chromophores will subsequently be incorporated into right- and left-handed sequences of oligonucleotides forming G-quadruplexes, in order to examine the chiroptical properties of the resulting smart photoresponsive systems. Moreover, we will synthesize chiral azobenzene derivatives, where two azobenzene motifs will be linked by a different length of polyethylene glycol. This approach will permit to find the most optimal length of the linker between two photochromic moieties to design light-responsive ligands recognizing higher order G-quadruplexes. This concept should pave the way toward new high-order G-motifs-based light-activated advanced materials.