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Oral Communication Yes / ~~No~~

Poster (A0 portrait) Presentation ~~Yes~~ / No

Poster + flash Presentation ~~Yes~~ / No

Title: Phenylazothiazole photoswitches on macromolecules for solar energy storage : photoisomerization and thermal back isomerization kinetics by MS

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Abstracts (max 400 words):

Molecules that undergo light-induced isomerization to metastable isomers can be used to store solar energy. Such systems are known as MOlecular Solar Thermal systems (MOST). Exposing photoswitching molecules to sunlight generates high energy photoisomers whose lifetime is considered as a key criterion for storage purpose. When energy is needed, the photoisomer is converted back to the stable form, releasing the excess energy under the form of heat. Azobenzenes (AB) with their E → Z photoisomerization are among the most widely studied molecular photoswitches although properties such as the storage enthalpy, half-life time and optical properties need to be improved. Two strategies are considered in our group to optimize azobenzene-based chromophores for MOST applications; *i.e.* (i) the substitution of one phenyl group by a thiazole moiety to red shift the absorption of the chromophores in the visible region, and (ii) the grafting of several azobenzene residues at selected positions along a polymer backbone to enhance the storage enthalpy and the metastable isomer half-life time via cooperating effects. Anchoring AB photoswitches on a peptoid chain is performed using an on-resin step-by-step synthetic procedure allowing

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to incorporate different side chains at selected positions. Two different residues are incorporated in our photoactive peptoids; i.e., (*S*)-phenylethylamine (*Nspe*) and (*E*)-4-(thiazol-2-yl-diazenyl) aniline (*N2tz*). Three peptoids have been successfully synthesized, namely *N2tzNspeNspe* (N-ter position), *NspeN2tzNspe* (center position) and *NspeNspeN2tz* (C-ter position). Their sequences were confirmed via tandem mass spectrometry (MS/MS) experiments, based on the B/Y, A/Y, and Side Chain Loss (SCL) fragmentation patterns. All peptoids were subjected to photo-illumination experiments. LC-MS experiments were carried out before and after irradiation to separate/identify/quantify the stereoisomers. The kinetics of thermal back-isomerization were studied by performing repeated LC-MS measurements while maintaining the peptoid methanolic solutions in the HPLC autosampler, kept in the dark and at a controlled temperature. *E* and *Z* isomers were mostly detected as protonated species $[MH]^+$. Extracted Ion Current (EIC) chromatograms were utilized to detect the stable and metastable isomer ions and determine the overtime evolution of their relative proportions. Repeating the kinetic measurements at different temperatures allows determining the kinetic parameters, including the activation enthalpy and entropy, of our MOST candidates, further affording evidences on the relaxation mechanisms.

To be sent (pdf file):

Oral : before June 30, 2025

to pascal.gerboux@umons.ac.be

Poster (+ flash) : before July 15, 2025

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