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Mass Spectrometry and Photochemical Study of Photoisomerization and Thermal Back-isomerization of Heteroaryl Azobenzenes anchored on Peptoids for the Chemical Storage of Solar Energy

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Summary: Storing renewable energies represents a major challenge in modern science. The most abundant energy source is undoubtedly the Sun. Several storage concepts have already been studied and among them, chemical storage with MOlecular Solar Thermal systems (MOST) appears promising though challenging.

Keywords: Solar Energy, Storage, Mass Spectrometry

Introduction

Molecules that undergo light-induced isomerization to a metastable isomer can be used to store solar energy. Such systems are known as MOlecular Solar Thermal systems. Exposing compound to sunlight generates a high energy photoisomer whose lifetime is considered as a key criterion for storage purpose. When energy is needed, the photoisomer is converted back to the stable compound, releasing the excess energy in the form of heat. Azobenzenes (ABs) with their E → Z photoisomerization are among the most widely studied molecular photoswitches. Properties such as storage enthalpy and half-life time need to be improved. To do so, grafting azobenzenes at selected positions all along a polymer backbone appears to be an elegant strategy to enhance these properties thanks to cooperative effects between the chromophores [1].

Experiment

At UMONS, two strategies to enhance the solar energy absorption, the storage enthalpy and the metastable isomer half-life time of MOST azobenzene-like candidates are considered; (i) the replacement of one phenyl group by a thiazolyl moiety is envisaged to red shift the absorption of the chromophores in the visible region [2], and (ii) the grafting of several azobenzene residues at selected positions all along the polymer backbone. Anchoring AB photoswitches on a peptoid chain is performed using an on-resin step-by-step synthetic procedure allowing to incorporate

different side chains at selected positions. Three different residues are incorporated in our photoactive peptoids; i.e. methylamine (*me*), (S)-phenylethylamine (*spe*) and (E)-4-(thiazol-2-ylidiazanyl) aniline (*azo*).

Results

Two peptoids have been successfully synthesized, namely NspeNazoNspe and NmeNazoNme, and their sequences are confirmed based on MSMS analysis. Both peptoids are subjected to photoillumination experiments. LC-MS experiments are carried out before and after irradiation to separate/identify/quantify the stereoisomers. Before irradiation, only the stable E-isomers are detected for both structures provided the peptoid solutions are protected against ambient light. After UV-vis irradiation, only the Z-isomers of the Nspe containing peptoid are detected, pointing to a fast retro isomerization of the Z-isomers of the methyl-containing peptoid.

Conclusions

With this work combining synthesis and photochemical characterization, we demonstrated that peptoids can be a good template to improve MOST properties of azobenzene. The *spe* side chains position greatly influence the half life time as opposed to methyl side chain. The stabilizing effect of the phenyl ring of the Nspe residue within the Z-isomers is currently tested by preparing defined sequence peptoids incorporating the Nazo, the Nspe and the Nme residues at key positions.

References

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