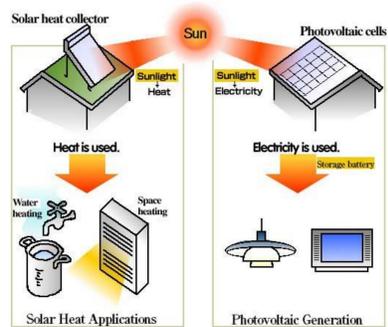


Mass Spectrometry and Photochemical Study of Photoisomerization and Thermal Back-isomerization of Substituted Azobenzenes anchored on Peptoids for the Chemical Storage of Solar Energy

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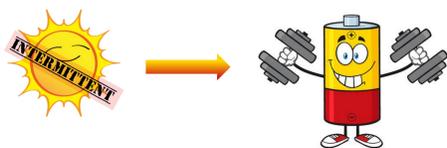
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Energy challenges: a matter of storage?



Sun as renewable energy source

Storage



MOlecular Solar Thermal systems (MOST)

To store solar energy, chemical storage appears to be a promising approach with systems known as MOST [1]. The working principle of those systems is based on iterative closed cycles of photoisomerization and back-isomerization between a parent compound and its metastable isomer (Figure 1). Energy is stored within the metastable isomer which possesses a certain half-life time and thermal energy is released during the thermal back-isomerization process [2] [3].

Azobenzenes with their E→Z photoisomerization are among the most widely studied molecular photoswitches and appear as good candidates. However, properties such as the storage enthalpy, spectroscopic properties and the half-life time need to be improved.

Charging process - Photoisomerization

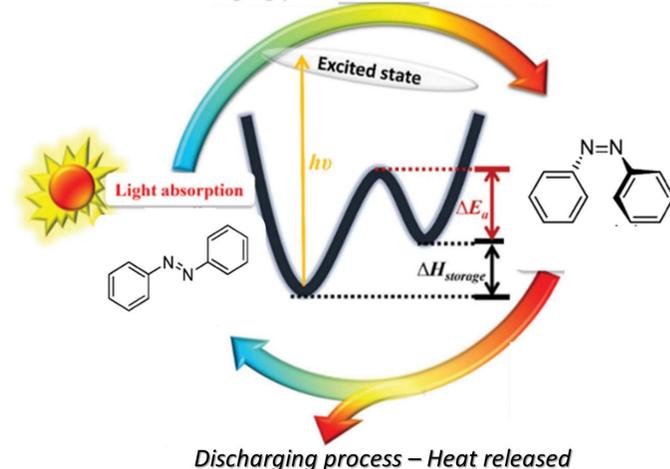


Figure 1. Working principle of a MOST system: the azobenzene case [3].

Improving azobenzene MOST properties: our strategy

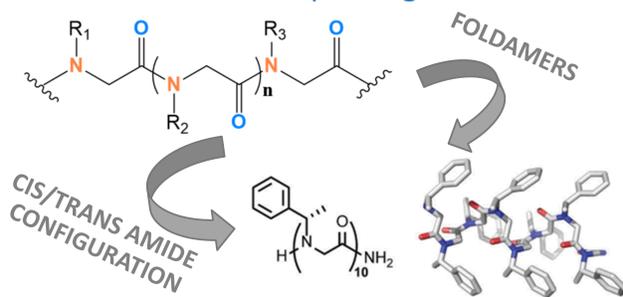


Figure 2. Primary structure of a peptoid.

Example of helical secondary structures with (S)-1-phenylethyl side chain [7].

At UMONS, two strategies are considered to optimize azobenzene-based chromophores for MOST applications; (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 [4], and (ii) the grafting of several azobenzene residues at selected positions all along a polymer backbone appears as an elegant strategy to enhance the storage enthalpy and the metastable isomer half-life time upon cooperating effects [5-6].

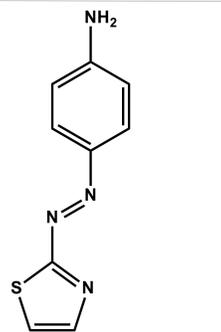
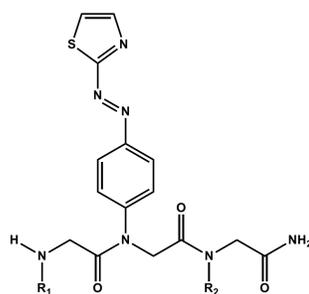
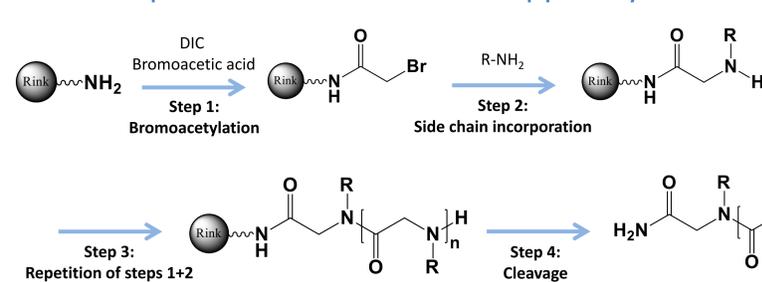
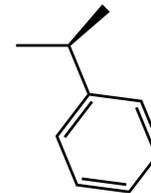


Figure 3. (E)-4-(thiazol-2-ylidiazenyl) aniline [4].

Peptoids of interest : solid support synthesis



R₁, R₂ = —CH₃ OR



4 Isomers

- NspeNazoNspe (1)
- NmeNazoNme (2)
- NspeNazoNme (3)
- NmeNazoNspe (4)

Structural characterization of the synthesized peptoids: MSMS spectra

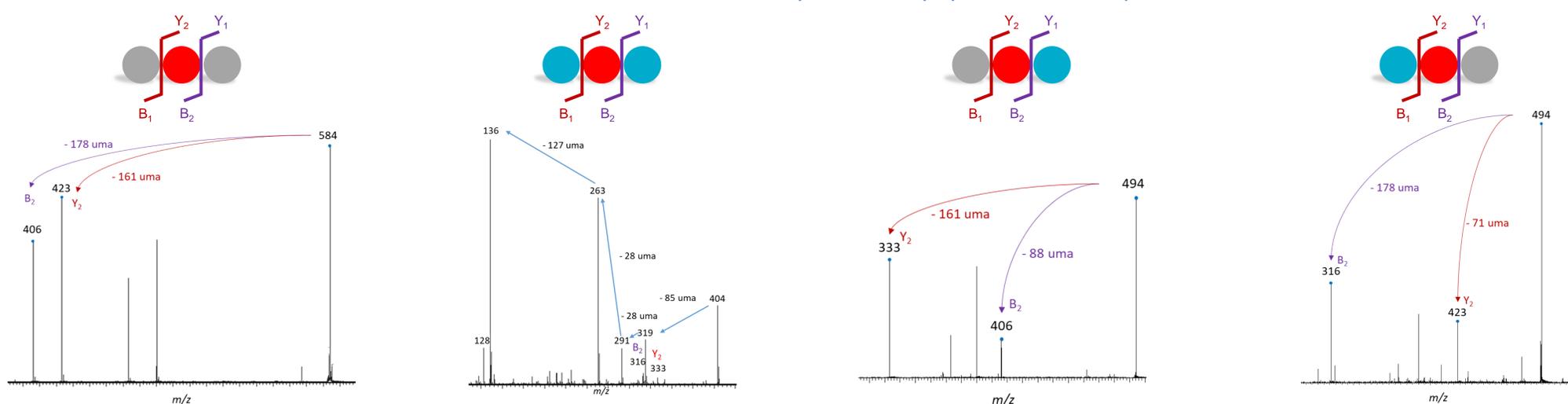


Figure 4. MSMS analyzes of peptoids 1-4 (Ecol = 12eV).

Photoisomerization experiments: LC-MS quantification of PSD

Peptoid solutions were irradiated with a lampe lightningcure LC8 L9588-03 visible lamp (ca. 400-700 nm) to induce azobenzene isomerization. After different irradiation times, solutions were analyzed by liquid chromatography (Waters Alliance 2695) coupled to mass spectrometry (Waters QToF Premier, ESI (+)) in order to discriminate stereoisomers and to quantify the photostationary state distribution (PSD).

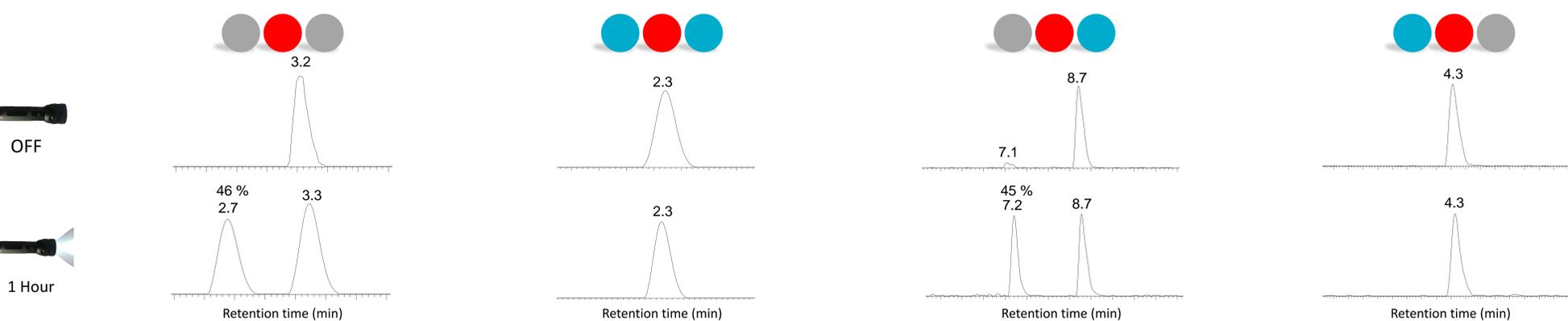


Figure 5. HPLC-MS analyzes of peptoids 1-4 after 1 hour of visible irradiation.

Half-life time:



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. In direct perspective of these results we can propose the synthesis of a positional isomer peptoids with Nazo in position 3 instead of position 2. In the same way, the Nme and Nspe chains will be alternated in order to confirm and better understand the interaction between the Nazo chain and the Nspe chain. Finally, theoretical modelling would allow us to really observe the possible interaction between the different side chains and to design an original peptoid with optimal properties.

Acknowledgments

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