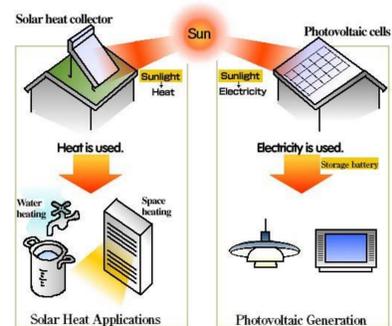


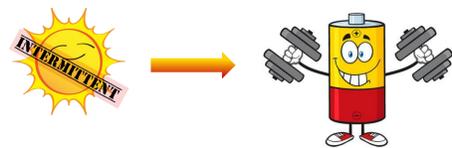


## Energy challenges: a matter of storage?



Sun as renewable energy source

Storage



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.

## MOlecular Solar Thermal systems (MOST)

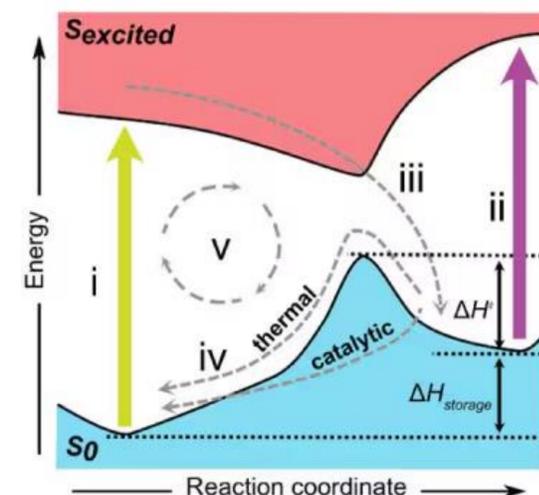


Figure 1. Working principle of MOST system: the azobenzene case: i) stable isomer absorbs sunlight and goes from ground state to excited state, ii) metastable isomer absorbs sunlight and goes from ground state to excited state, iii) deexcitation from the excited state to the metastable isomer ground state, iv) thermal or catalytic back-isomerization, v) repeat cycle [4].

## Improving azobenzene MOST properties: our strategy

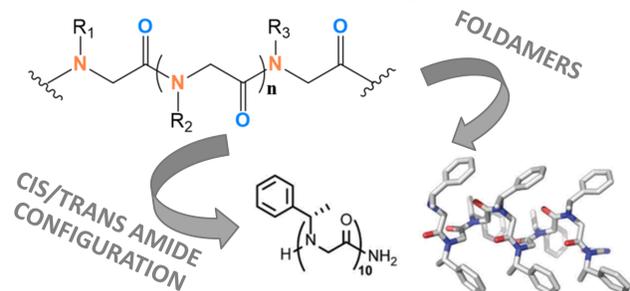


Figure 2. Primary structure of a peptoid.

Example of helical secondary structure with (S)-1-phenylethyl side chain [8].

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 [5], 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 [6-7].

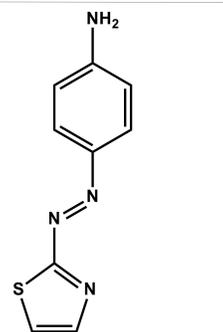
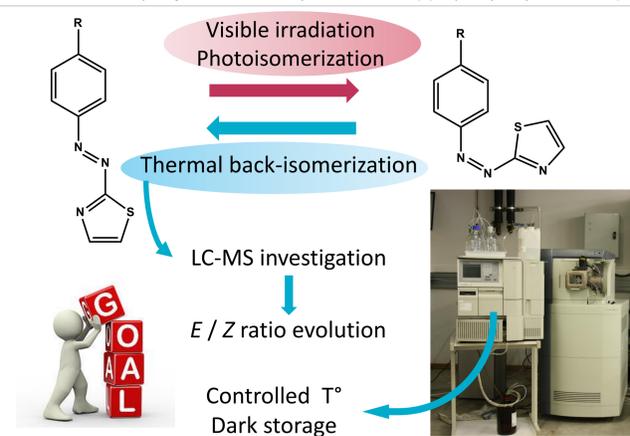
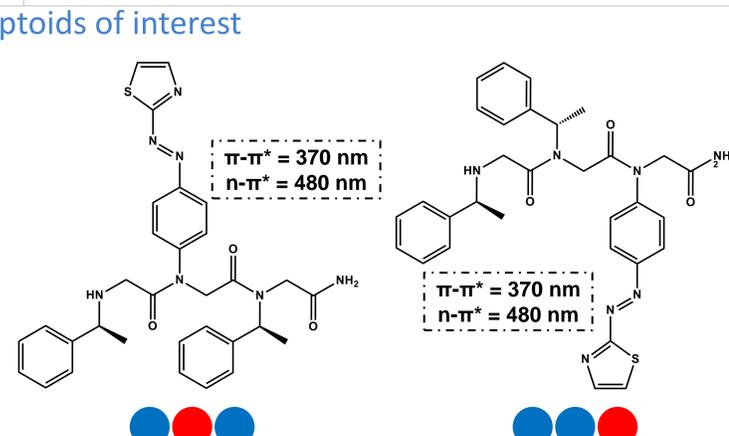
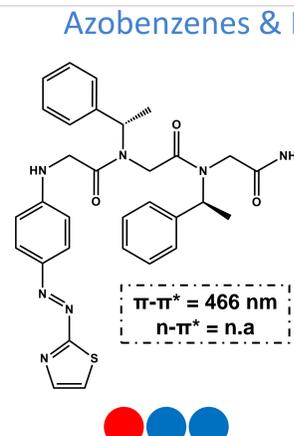
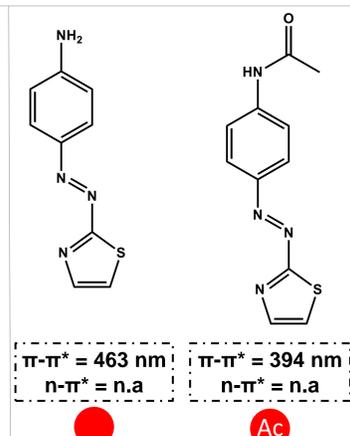


Figure 3. (E)-4-(thiazol-2-ylidiazene)aniline [5].

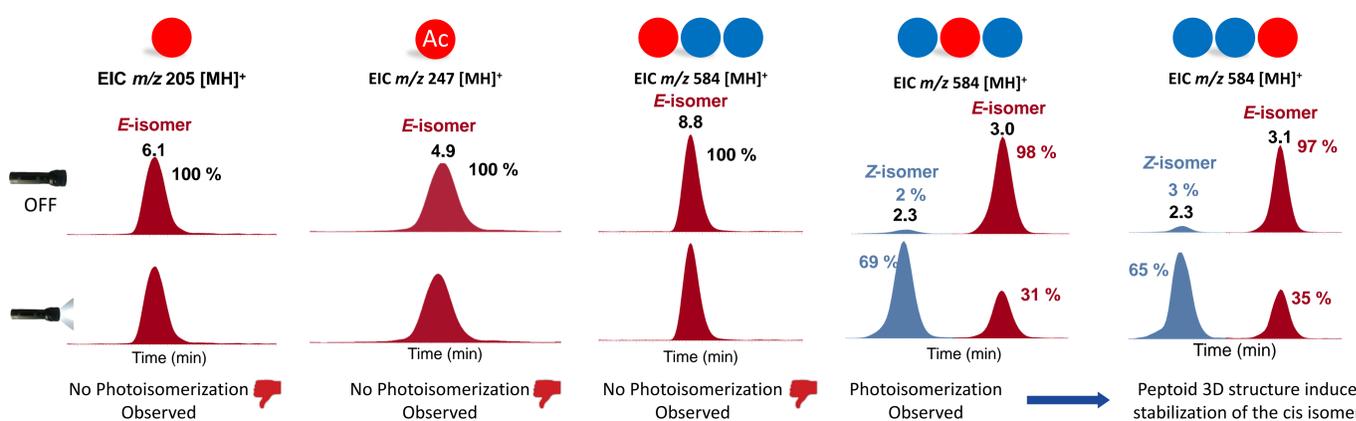


## Azobenzenes & Peptoids of interest



## LC-MS analysis: position effect

Azobenzene derivative solutions were irradiated with a lightningcure LC8 L9588-03 Visible lamp (ca. 350 - 800 nm) to induce azobenzene isomerization in MeOH at 20°C. 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).



## Kinetics study: Kinetic parameter calculation

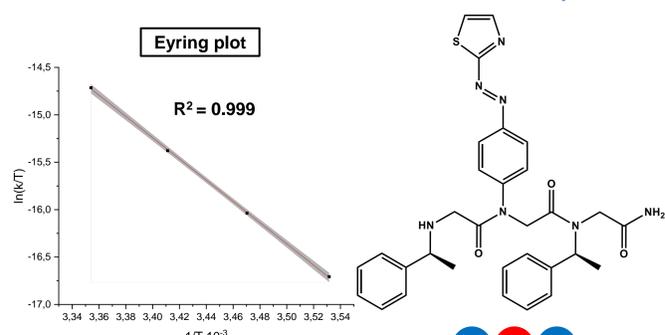


Figure 4. Eyring plot for the NspeNthiaNspe thermal back-isomerization in MeOH.

$$\Delta H^\ddagger = 93.1 \pm 0.9 \text{ kJ.mol}^{-1}$$

$$\Delta S^\ddagger = -7.7 \pm 3 \text{ J.mol}^{-1} \text{ K}^{-1}$$

$$\Delta G^\ddagger (20^\circ\text{C}) = 95.36 \pm 1.7 \text{ kJ.mol}^{-1}$$

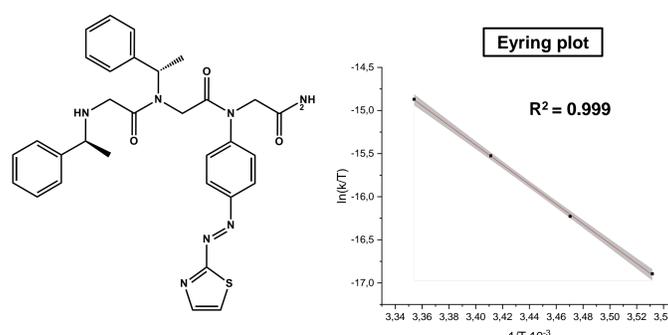


Figure 5. Eyring plot for the NspeNspeNthia thermal back-isomerization in MeOH.

$$\Delta H^\ddagger = 95.1 \pm 1.1 \text{ kJ.mol}^{-1}$$

$$\Delta S^\ddagger = -2.3 \pm 4 \text{ J.mol}^{-1} \text{ K}^{-1}$$

$$\Delta G^\ddagger (20^\circ\text{C}) = 95.76 \pm 2.3 \text{ kJ.mol}^{-1}$$

## Back-isomerization at 20°C: LC-MS monitoring

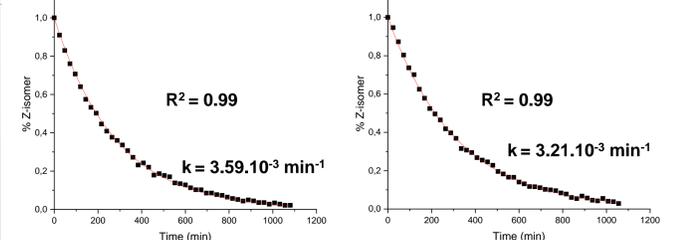
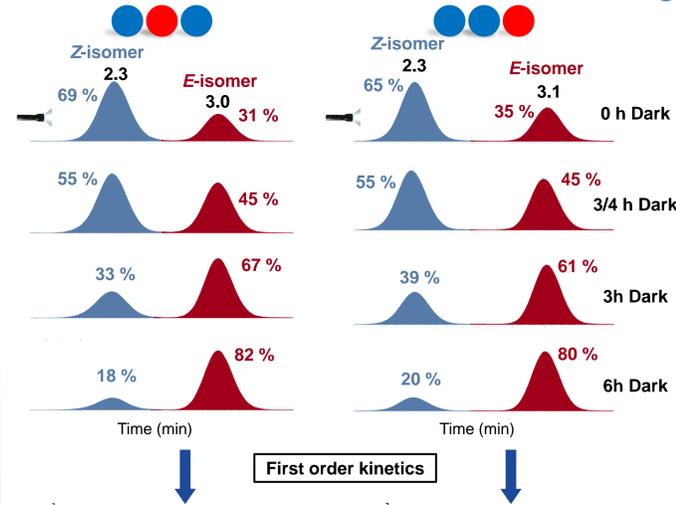


Figure 3. Thermal back-isomerization of NspeNthiaNspe and NspeNspeNthia at 20 °C in MeOH.

T (°C)	k <sub>moy</sub> (10 <sup>-5</sup> s <sup>-1</sup> )	t <sub>1/2</sub> (h)	k <sub>moy</sub> (10 <sup>-5</sup> s <sup>-1</sup> )	t <sub>1/2</sub> (h)
10	1.57 ± 0.02	12.25 ± 0.19	1.30 ± 0.02	14.7 ± 0.22
15	3.13 ± 0.06	6.16 ± 0.12	2.58 ± 0.06	7.46 ± 0.18
20	6.14 ± 0.15	3.13 ± 0.08	5.30 ± 0.04	3.63 ± 0.03
25	12.1 ± 0.5	1.59 ± 0.07	10.4 ± 0.16	1.85 ± 0.03

## Conclusions

With this work combining synthesis and LC-MS characterization, we demonstrated that heteroaryl azobenzene enhances spectroscopic properties with a bathochromic shift but not enough to reach visible wavelengths. Visible range of wavelengths could be reached with heterocyclic substitutions. We also demonstrate that peptoids can be a good template to improve azobenzene MOST properties, peptoids with azobenzene in centre position and C<sub>ter</sub> position enhance MOST properties and more specifically the half-life time of the cis-isomer which goes from none observable to measurable with LC-MS analysis. With LC-MS kinetic analyses performed at different temperatures we were able to determine kinetic parameters. The next step in this study is to perform theoretical modelling to observe the possible interactions between the different side chains and understand how peptoids stabilize cis isomer.

## Acknowledgments

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