Peptoids as Promising Azobenzene Support for the Chemical Storage of Solar Energy

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Introduction: a matter of storage …

Storing solar energy represents a major challenge in modern science. Several storage concepts have already been studied and among them, chemical storage with **MO**lecular **S**olar **T**hermal systems (**MOST**) appears promising though challenging [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 [1,2]. Among the MOST systems, the azobenzene chromophore with its E → Z photoisomerization has been largely explored (***Figure 1***). However, the properties of the azobenzene compounds must be improved for MOST applications, especially due to the low storage enthalpy (ΔE) and half-live times ($t_{1/2}$) encountered to date for these molecules [2,3].

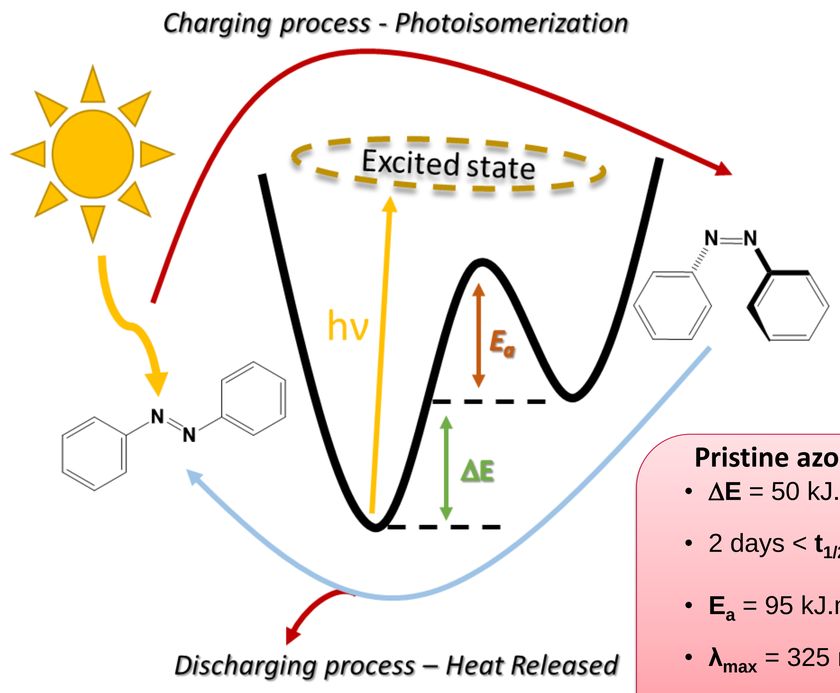


Figure 1. *Working principle of a MOST system: the azobenzene case.*

Improving azobenzene MOST properties: our strategy

Pristine azobenzene[1-3]
- ΔE = 50 kJ.mol^{-1}
- 2 days < $t_{1/2}$ < 4 days
- E_a = 95 kJ.mol^{-1}
- λ_{max} = 325 nm
- Photostationary state

Literature → *Incorporation on a macromolecule*

Close-packing and cooperative effects: ΔE, E_a and $t_{1/2}$ improved

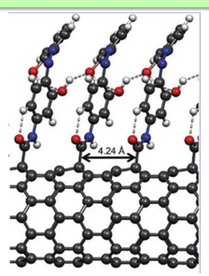


Figure 2. *Carbon nanotubes as templates for azobenzenes [4].*

This work → *Our backbone*

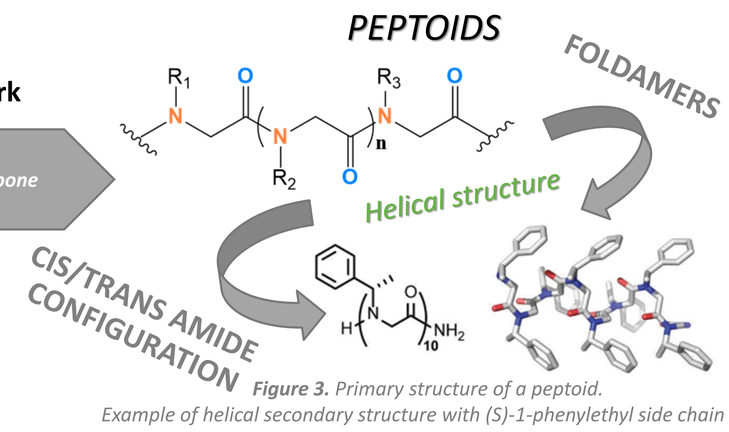
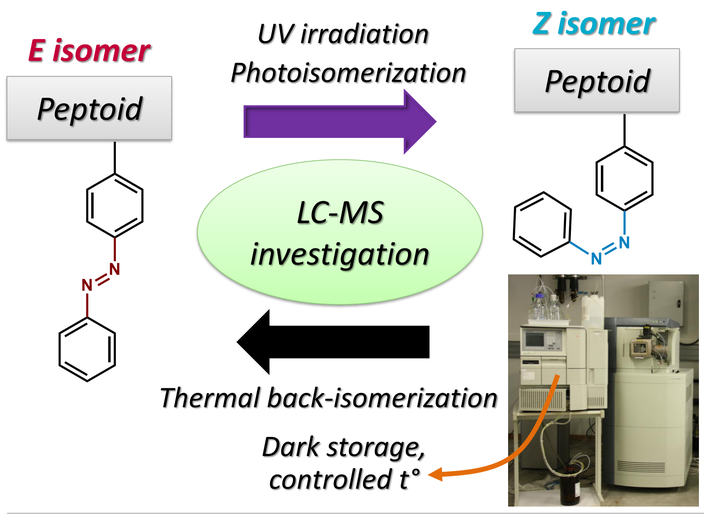
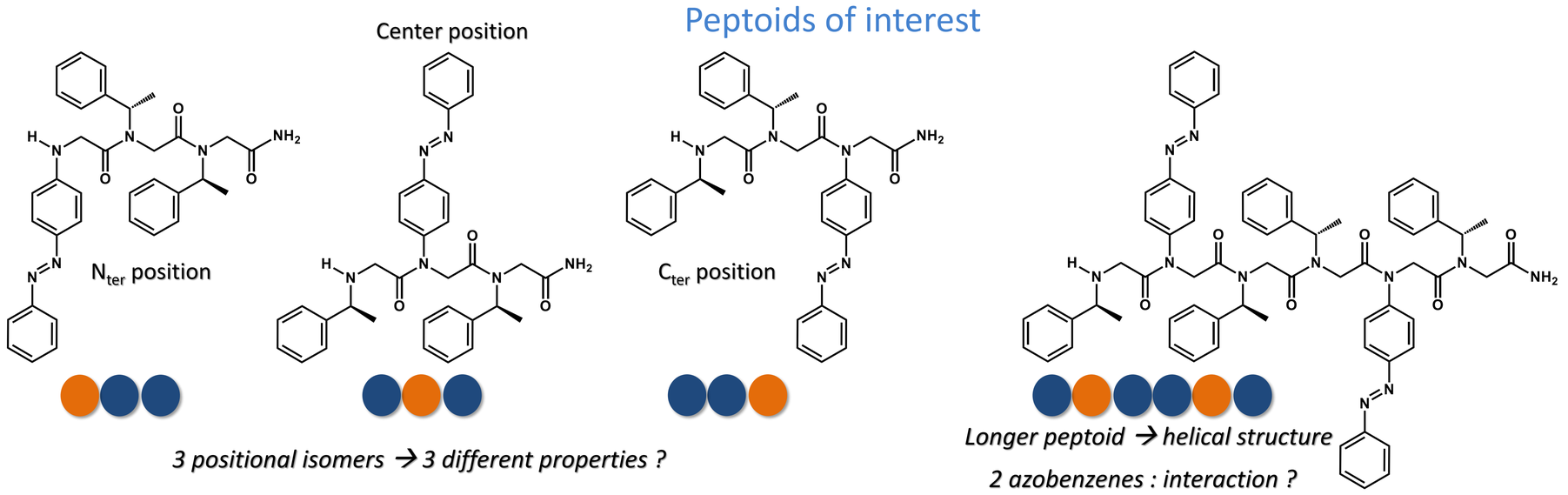


Figure 3. *Primary structure of a peptoid. Example of helical secondary structure with (S)-1-phenylethyl side chain [5].*

Goal of the study



Peptoids of interest



Position effect

Methanol, 20 °C

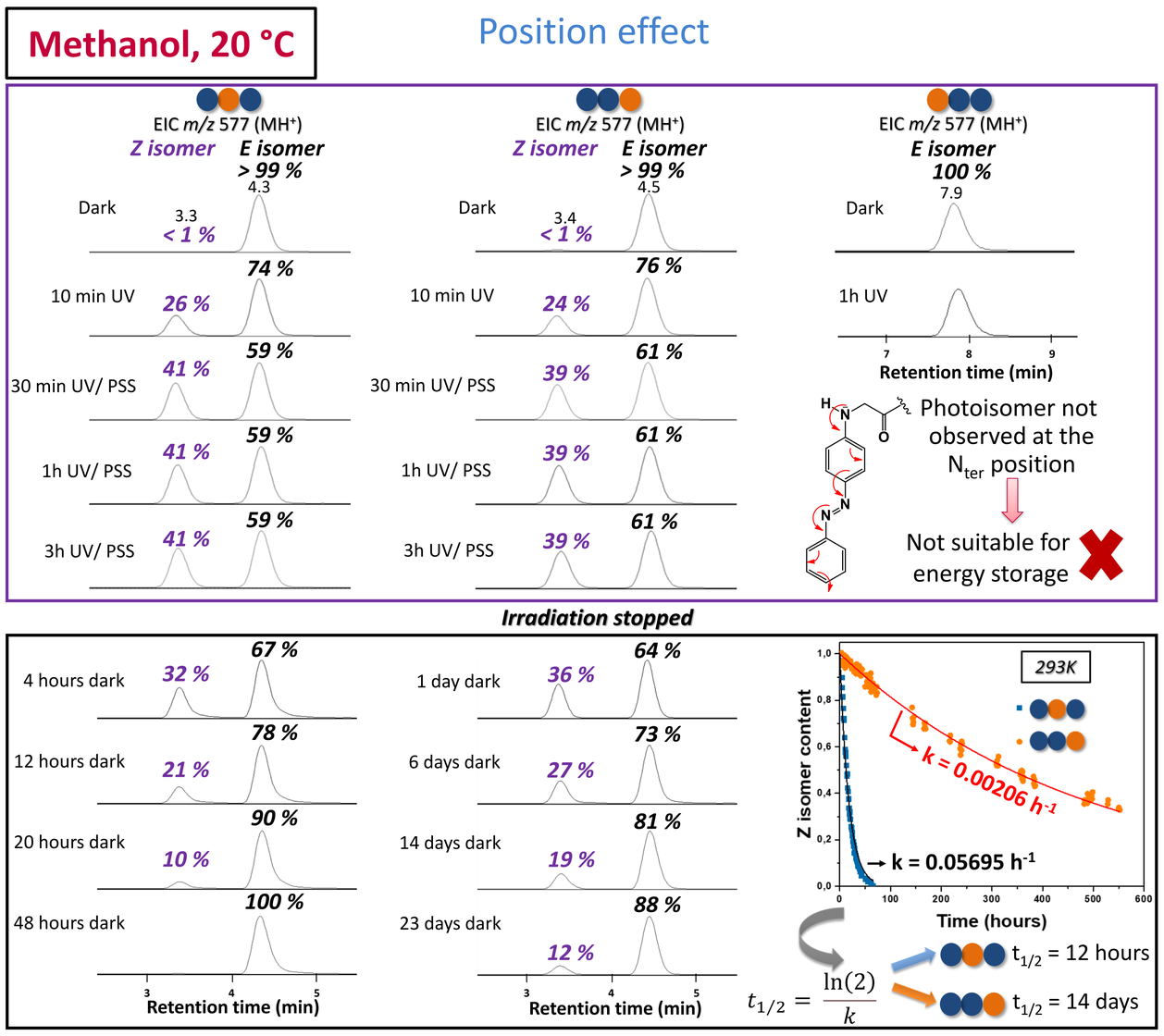
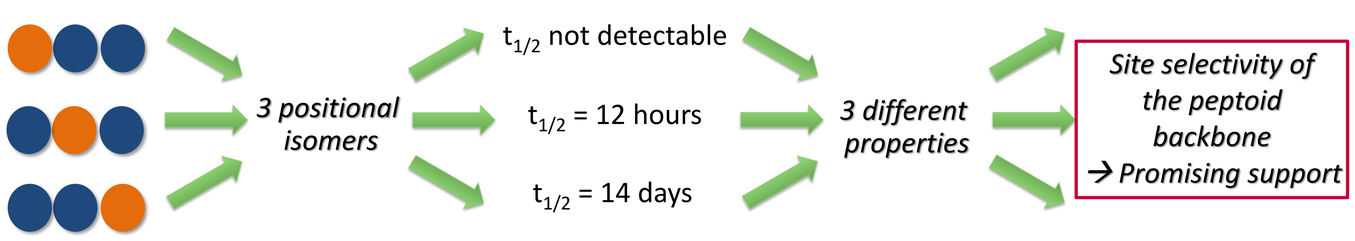
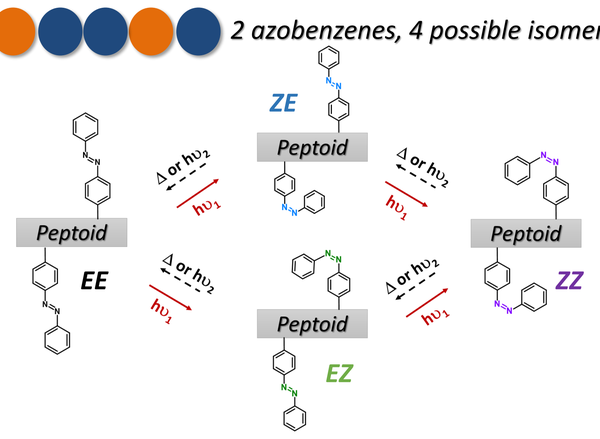


Figure 4. *LC-MS analysis (Extracted Ion Current (EIC) chromatograms of the $[M+H]^+$ ions at m/z 577) for the three peptoids. Purple box: photoisomerization using Arimed B6 lamp. Black box: thermal back-isomerization processes investigation while storing the peptoid solutions in the HPLC autosampler.*

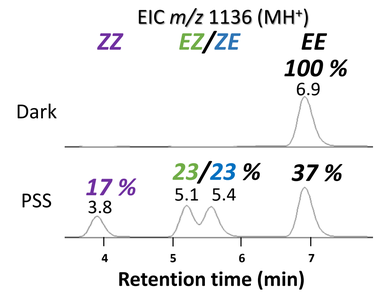


Multi-azo peptoids: interaction between the chromophores ?

2 azobenzenes, 4 possible isomers :



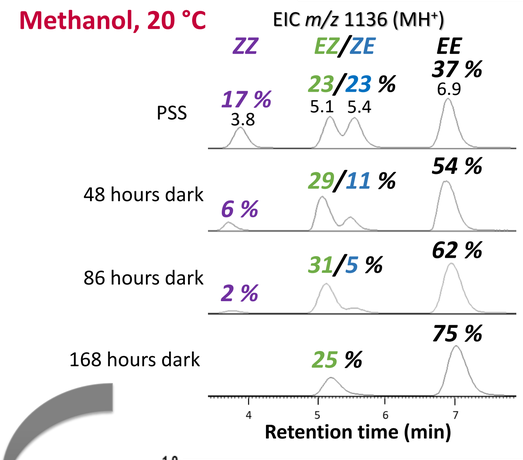
Photoisomerization ?



40 % of Z isomers
→ Photoisomerization preserved

What about the thermal back-isomerization ?

Methanol, 20 °C



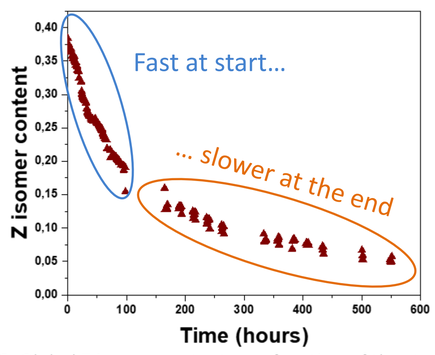
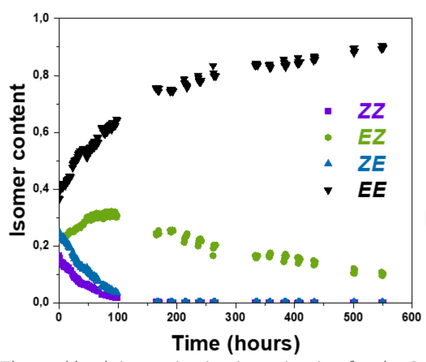


Figure 6. *Global Z isomer content as a function of the storage time.*

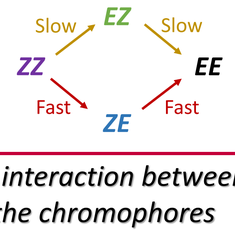


Two different kinetics

k_1 : 0.019 h^{-1} → $t_{1/2}$ = 36 h → *Position 2*

k_2 : 0.0026 h^{-1} → $t_{1/2}$ = 11 days → *Position 5*

Isomer identification



No interaction between the chromophores at these positions

Figure 5. Up: *Thermal back-isomerization investigation for the 6-units peptoid through the EIC of the $[M+H]^+$ ions at m/z 1136. Down: plot of each isomer content as a function of the storage time at 20 °C.*

Conclusions

In this work, we used peptoids as azobenzene support to store solar energy in the context of MOlecular Solar Thermal systems (MOST). With the development of a LC-MS based method, we extracted interesting properties especially a high site selectivity from the peptoid backbone observed with simple systems. Indeed, depending on the anchoring position, $t_{1/2}$ ranging from not detectable to 14 days were obtained for the azobenzene. A peptoid containing 2 chromophores was also investigated, and the LC separation prior to MS analysis allowed us to identify the four isomers but also to evidence the absence of interactions between the azobenzenes at these positions. This study paves the way for future development in solar energy storage.

Acknowledgements

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References

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