

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 MOlecular Solar Thermal 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-life times ($t_{1/2}$) encountered to date for these molecules [2,3].

Improving azobenzene MOST properties: our strategy

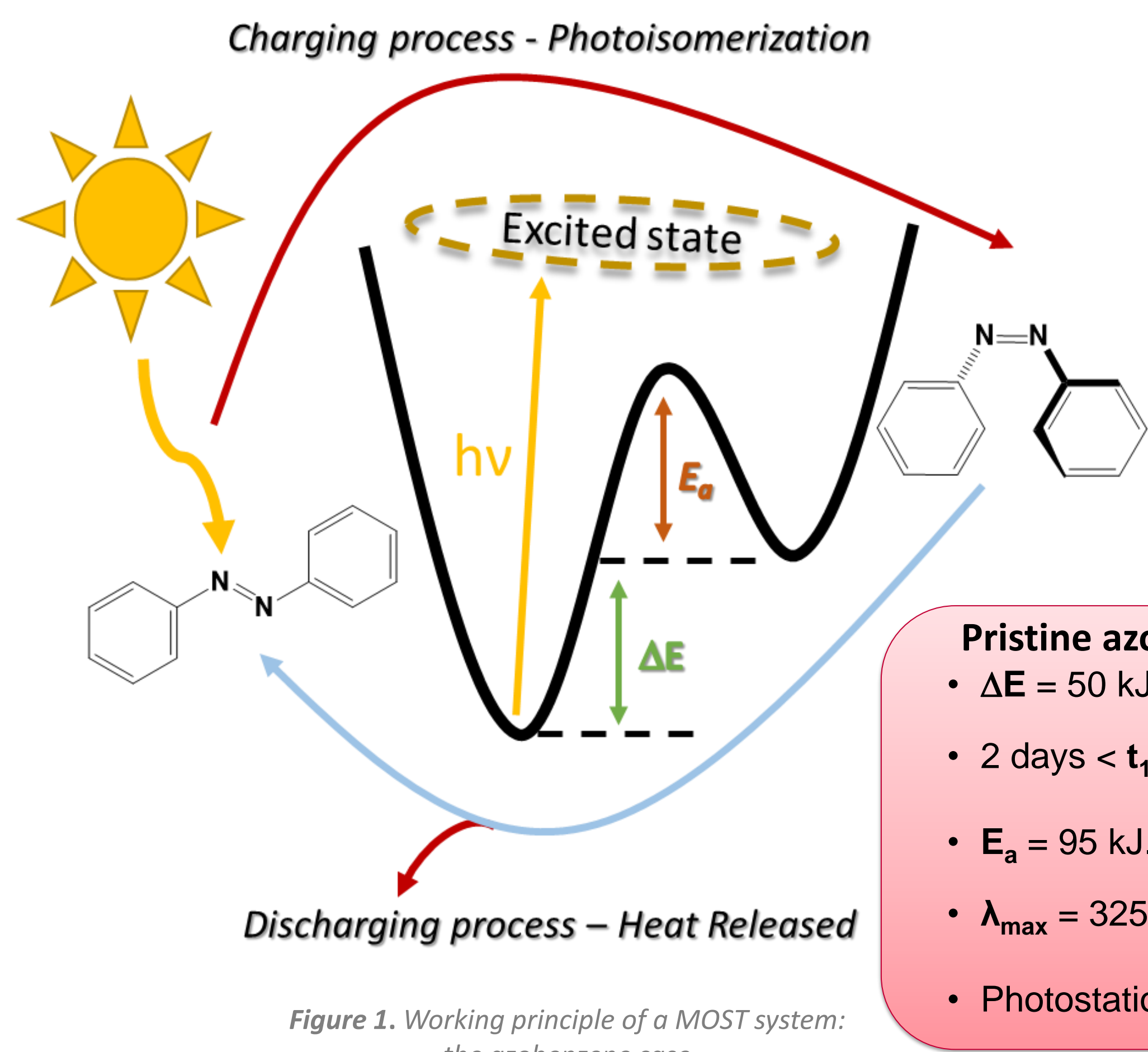


Figure 1. Working principle of a MOST system: the azobenzene case.

Pristine azobenzene^[1-3]

- $\Delta E = 50 \text{ kJ.mol}^{-1}$
- 2 days < $t_{1/2}$ < 4 days
- $E_a = 95 \text{ kJ.mol}^{-1}$
- $\lambda_{\text{max}} = 325 \text{ nm}$
- Photostationary state

Literature

Incorporation on a macromolecule

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

This work

Our backbone

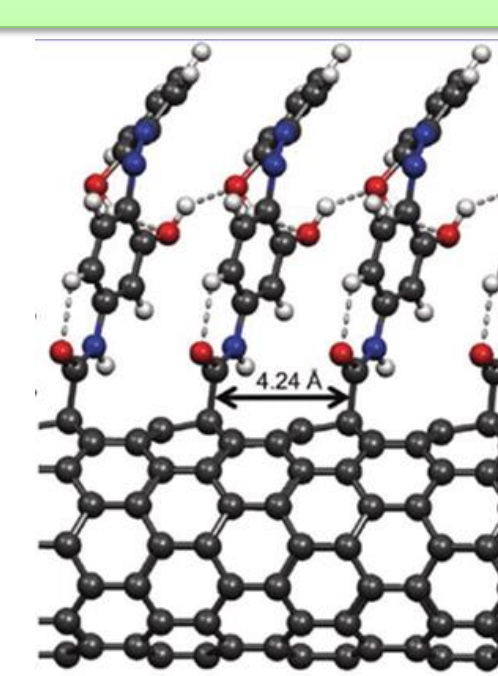


Figure 2. Carbon nanotubes as templates for azobenzenes [4].

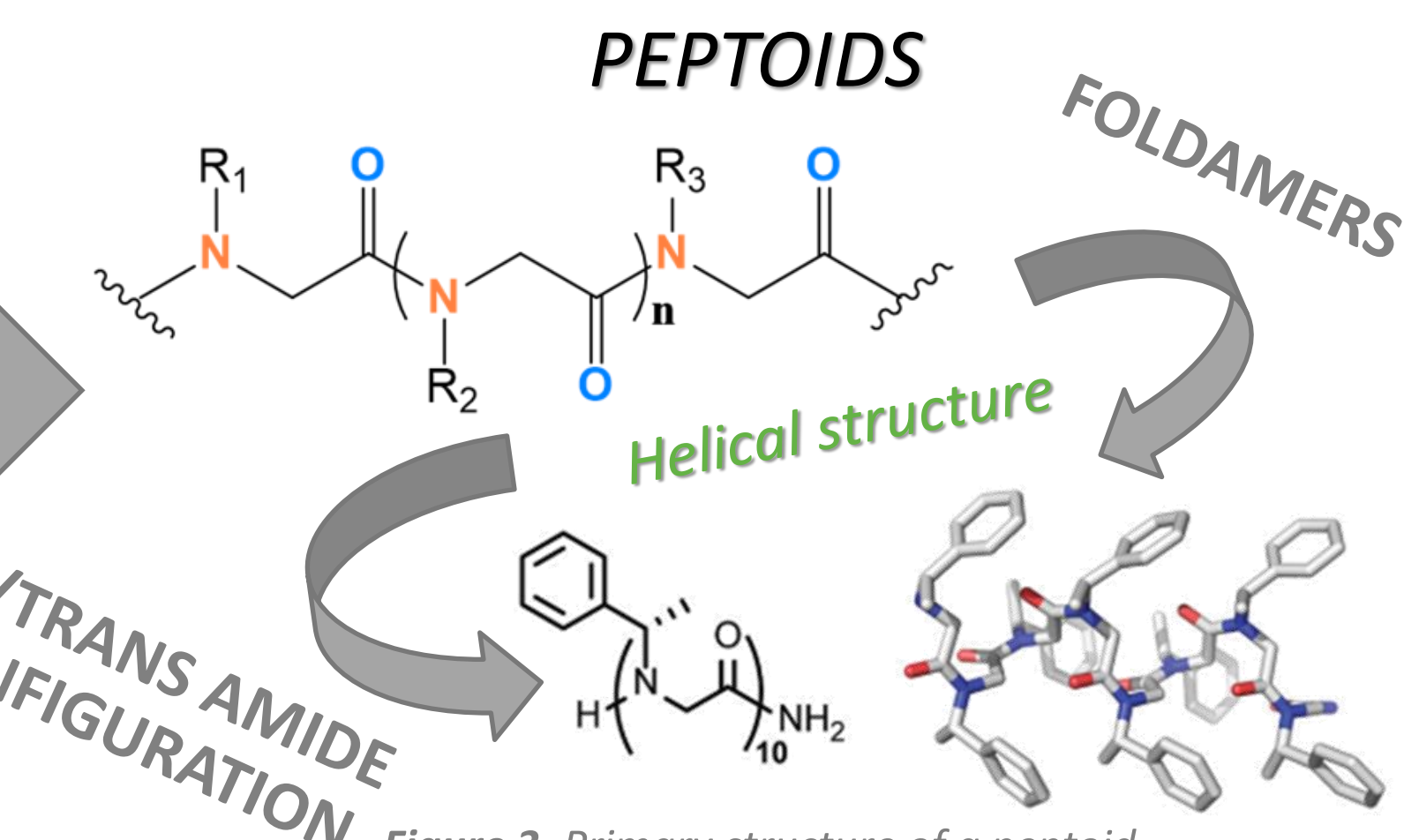
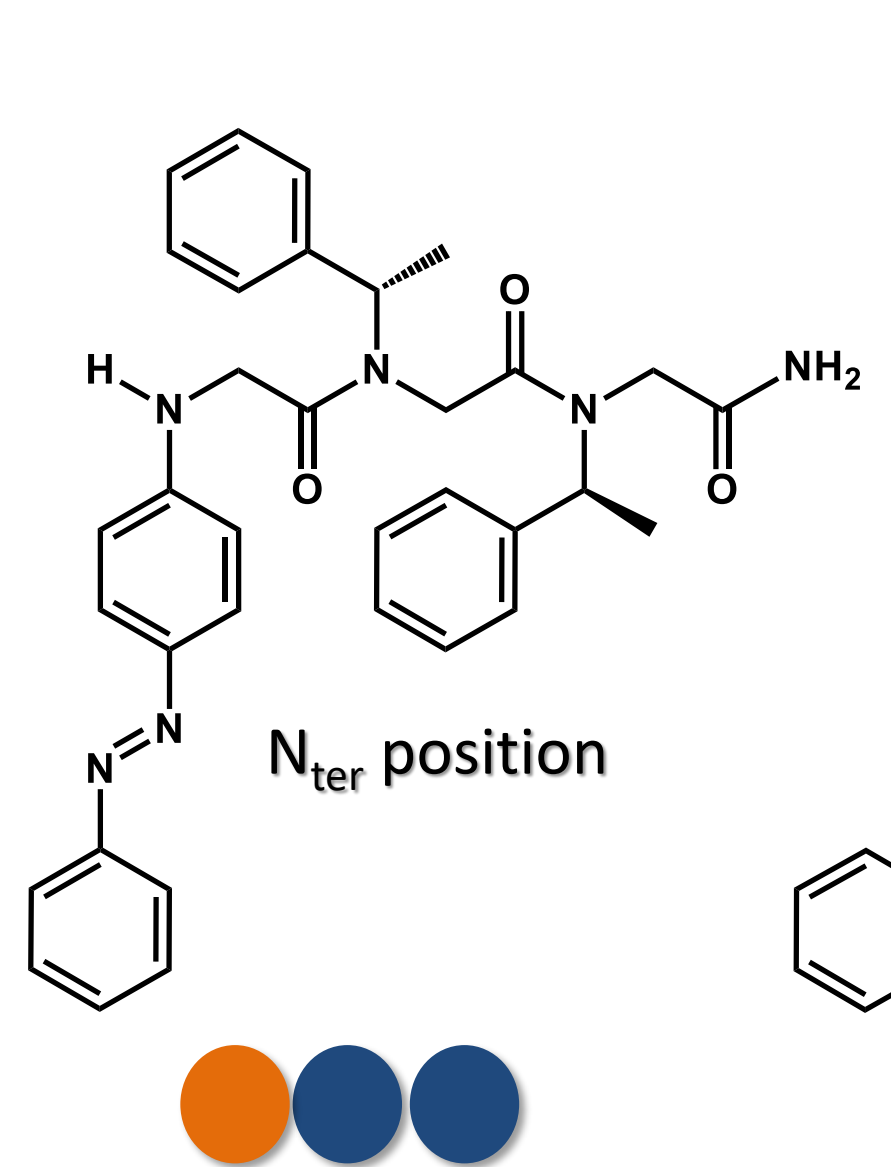
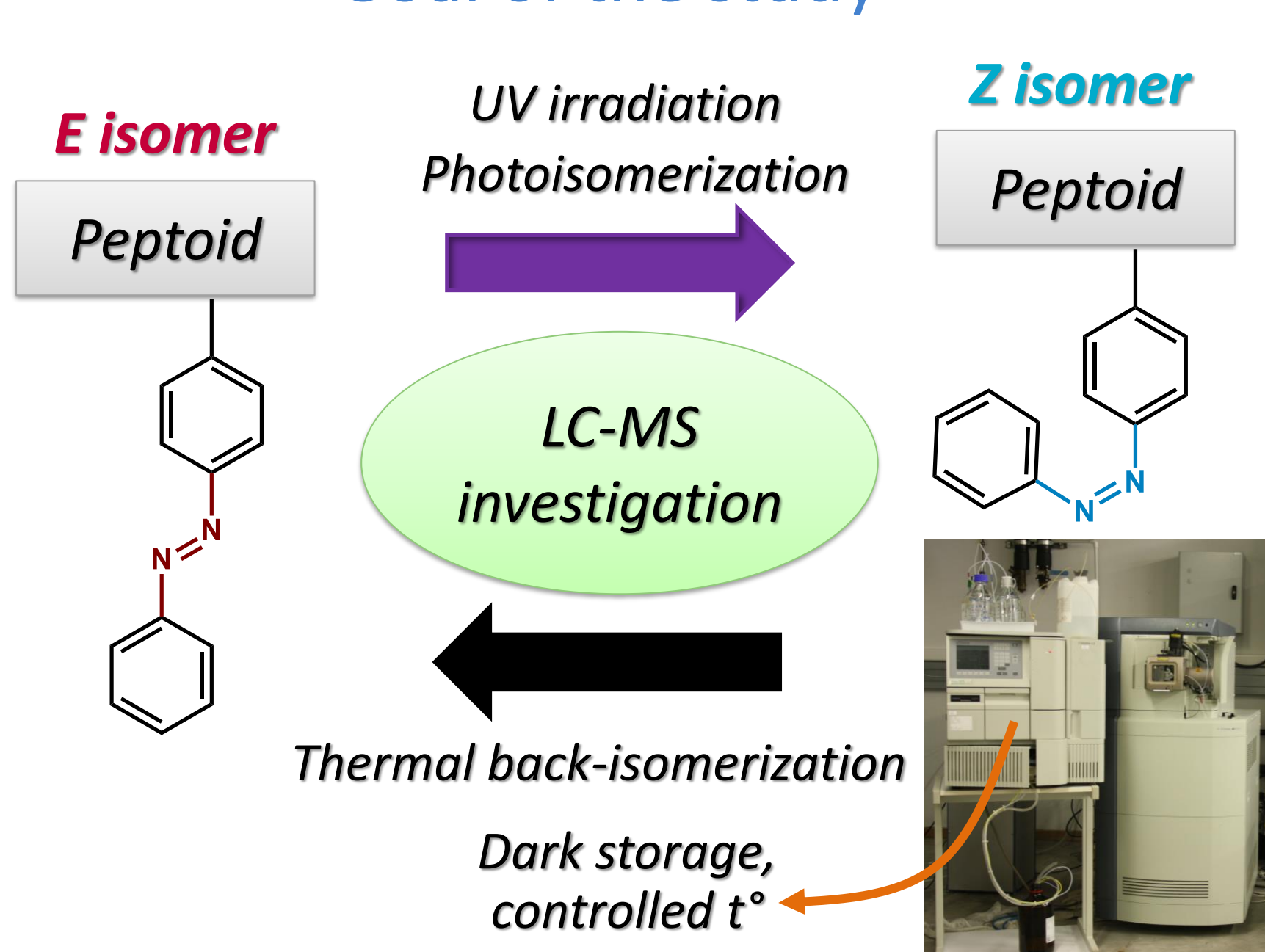


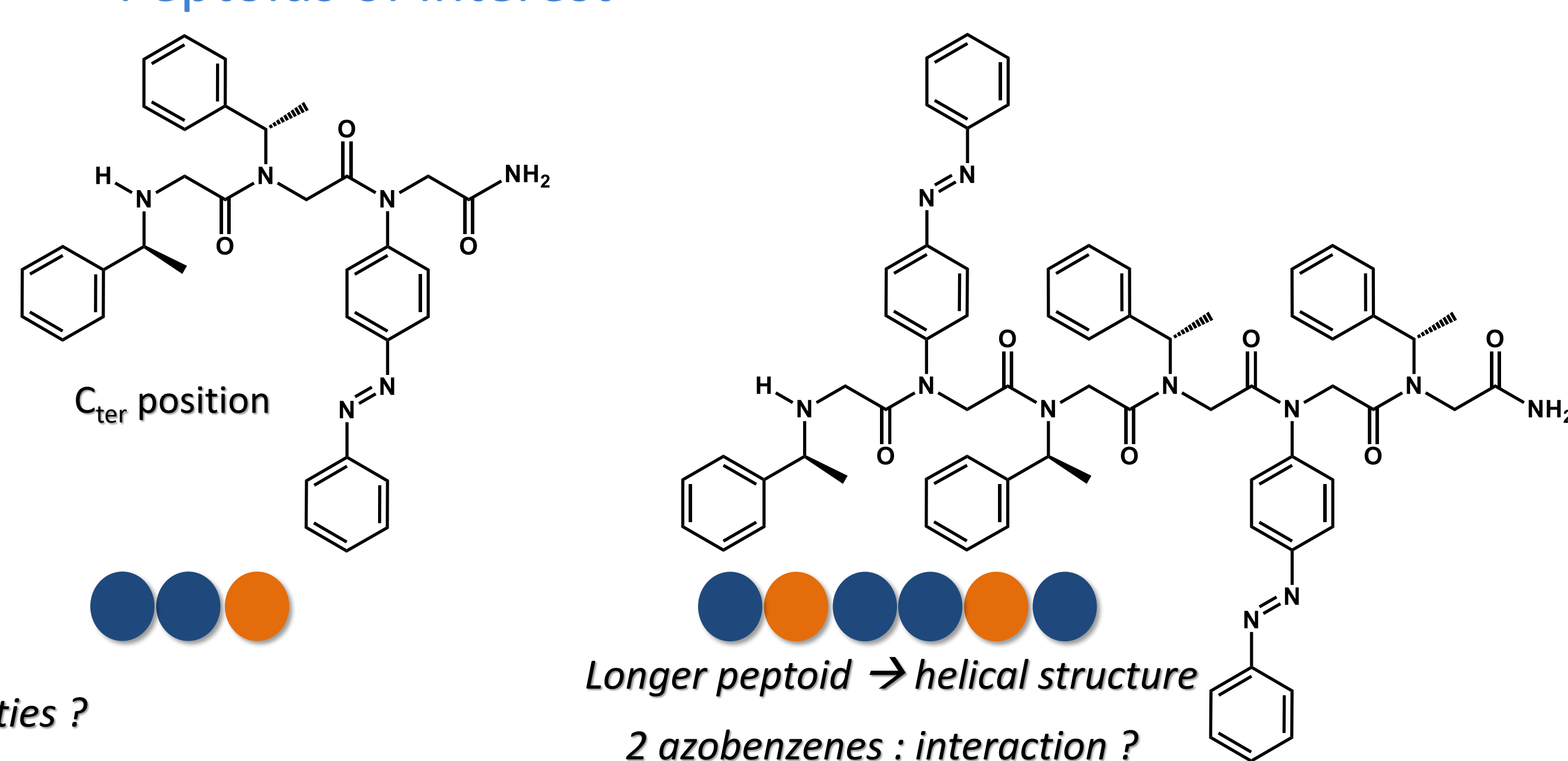
Figure 3. Primary structure of a peptoid. Example of helical secondary structure with (S)-1-phenylethyl side chain [5].

Goal of the study



3 positional isomers → 3 different properties ?

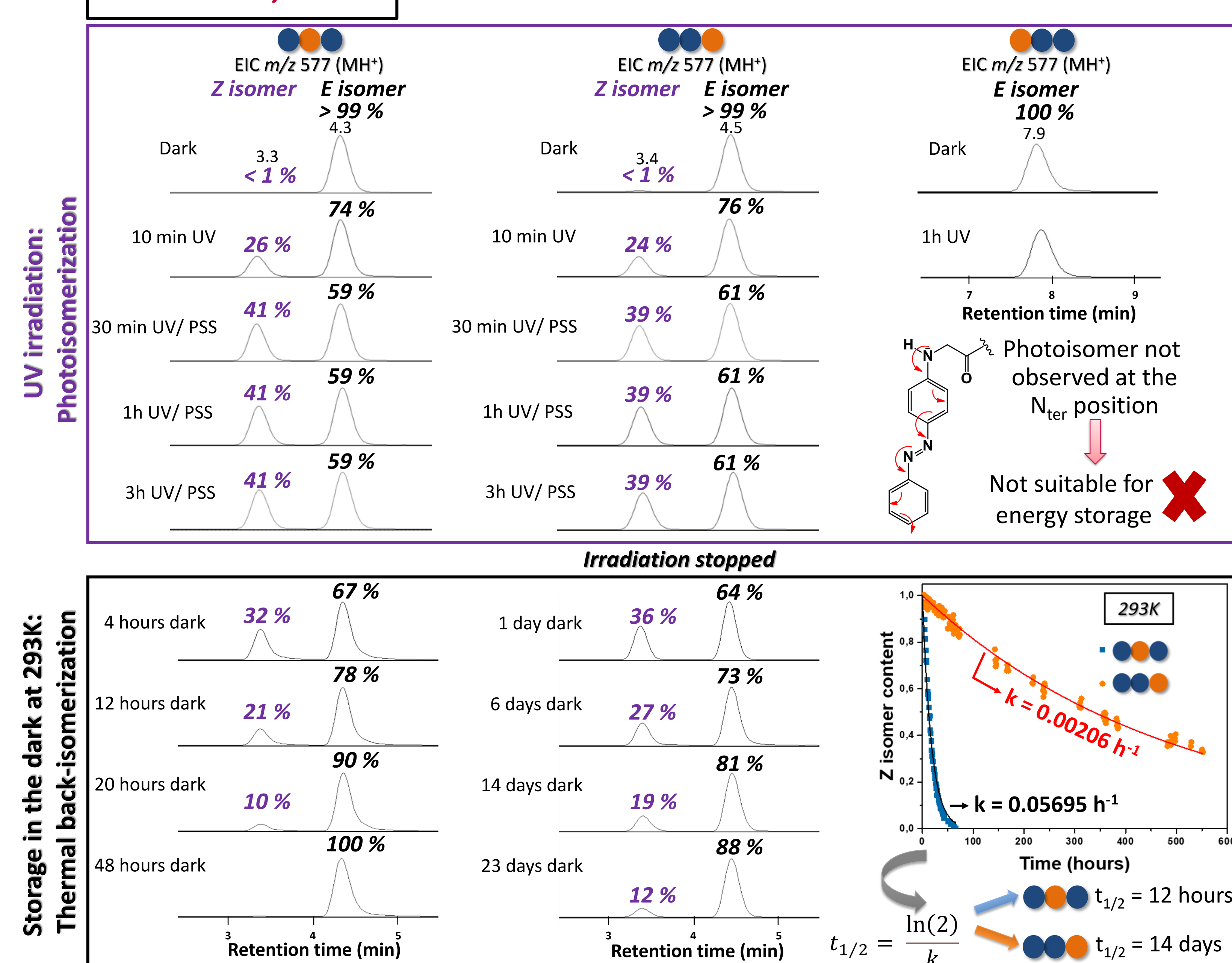
Peptoids of interest



Longer peptoid → helical structure
2 azobenzenes : interaction ?

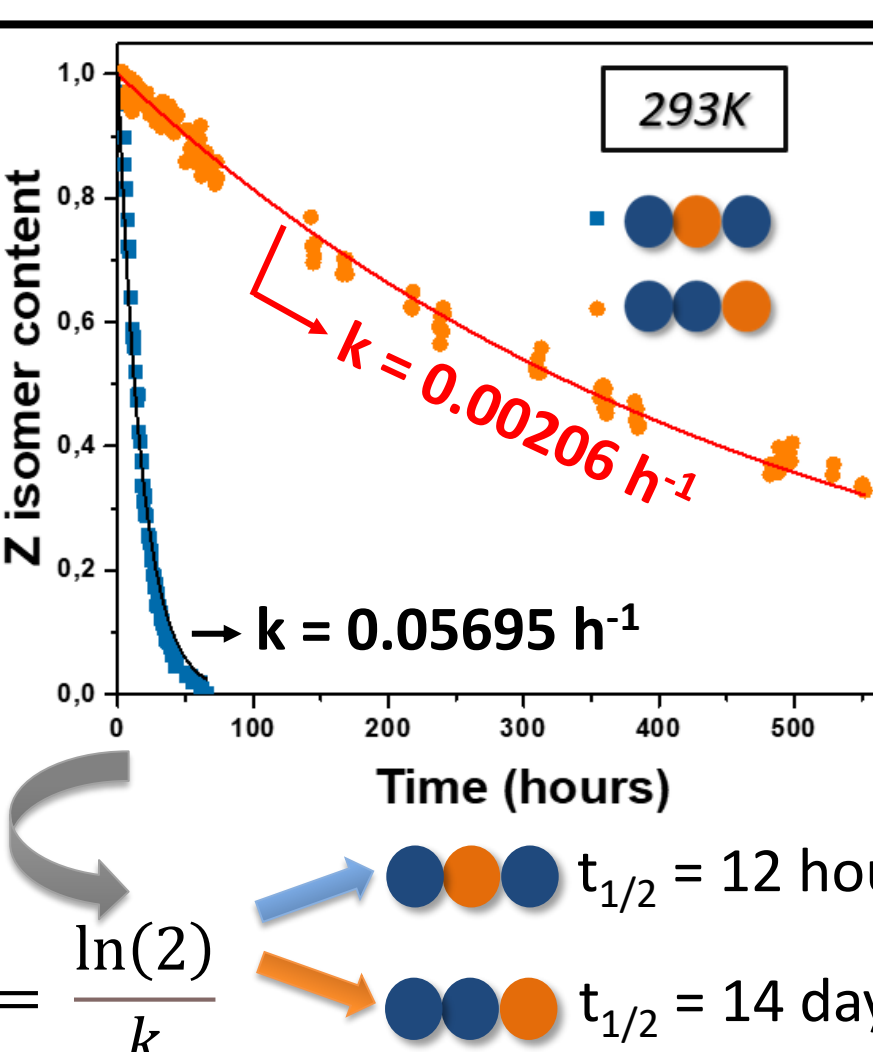
Methanol, 20 °C

Position effect



Photoisomer not observed at the N_{ter} position
Not suitable for energy storage ❌

Irradiation stopped



Multi-azo peptoids: interaction between the chromophores ?

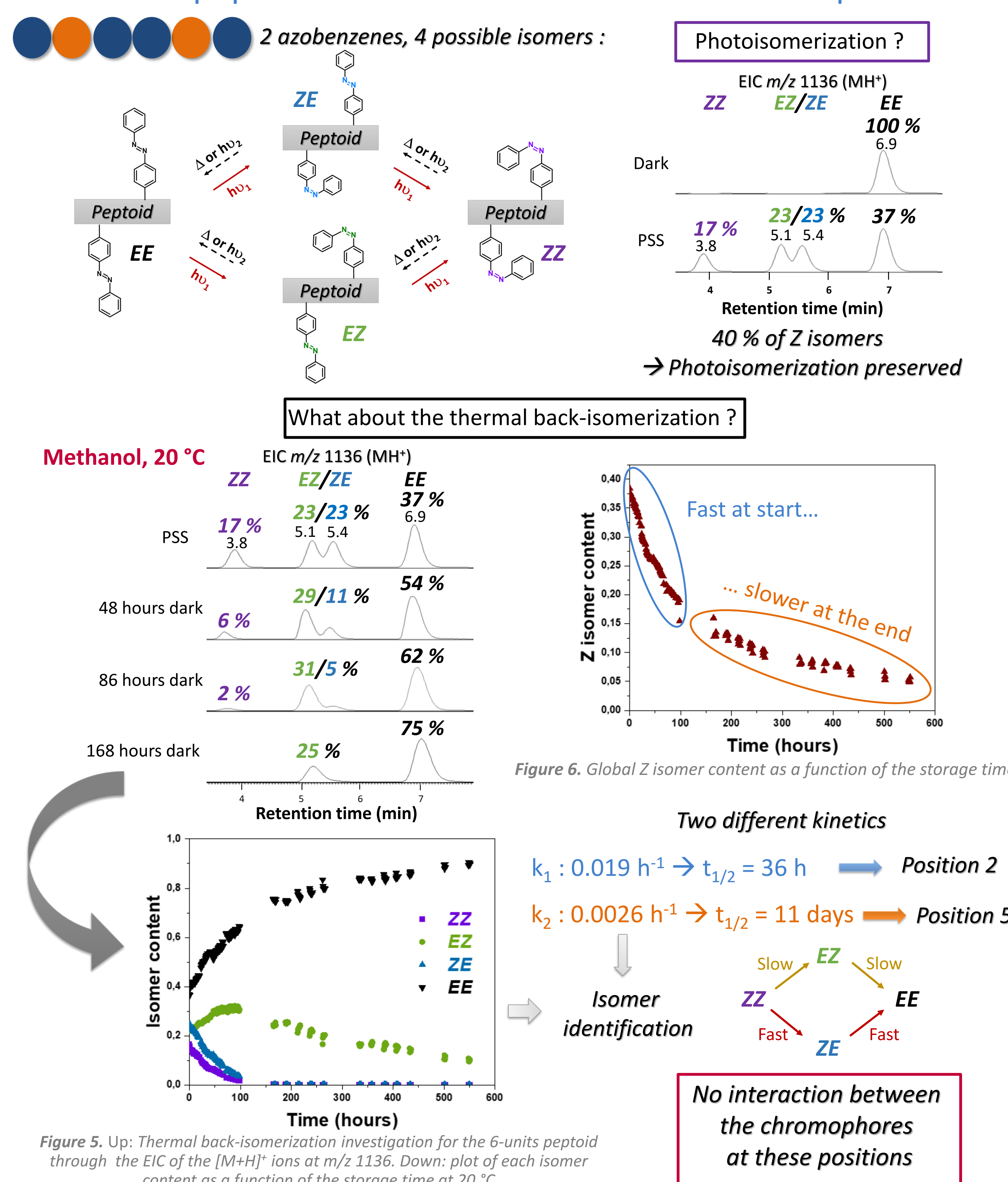


Figure 6. Global Z isomer content as a function of the storage time.

Two different kinetics

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

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

Isomer identification

Slow EZ Slow EE
Fast ZE Fast

No interaction between the chromophores at these positions

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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