# Mass Spectrometry Study of the Photoisomerization and Thermal Back-Isomerization of Azobenzene-Functionalized Peptoids for the Chemical Storage of Solar Energy

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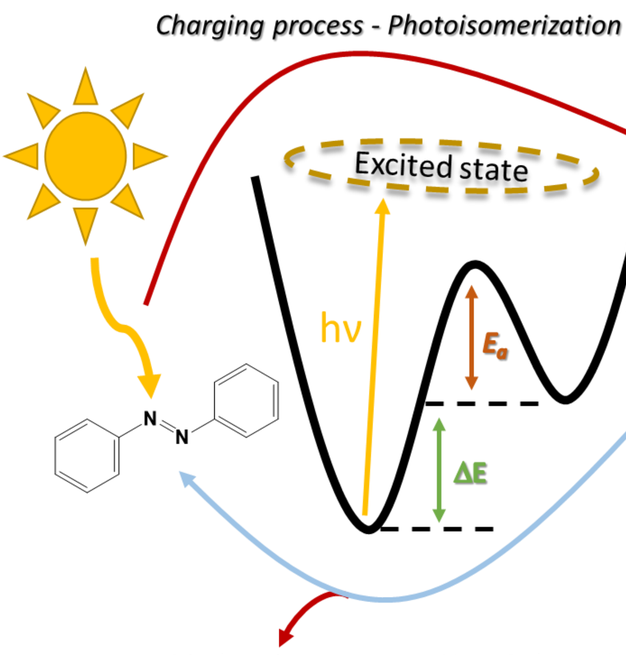



*Figure 1. Working principle of a MOST system: the azobenzene case.*

## 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].

## Improving azobenzene MOST properties: our strategy

**Literature** → *Incorporation on a macromolecule* → Close-packing and cooperative effects: ΔE, $E_a$ and $t_{1/2}$ improved → **This work** → *Our backbone*

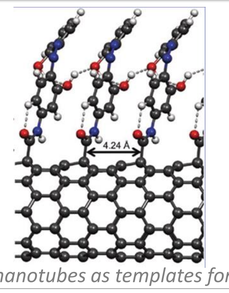



*Figure 2. Carbon nanotubes as templates for azobenzenes [4].*

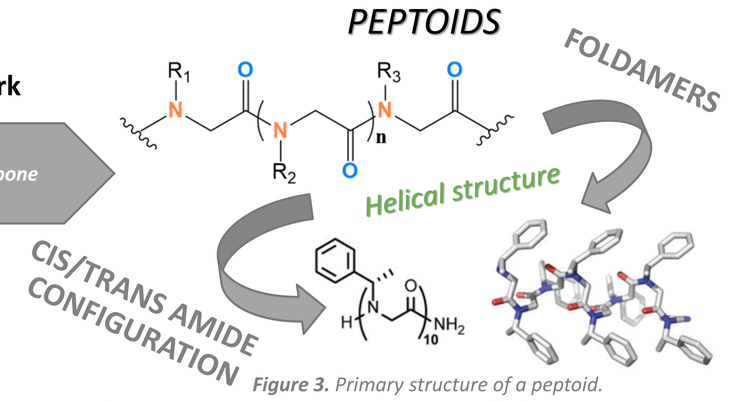
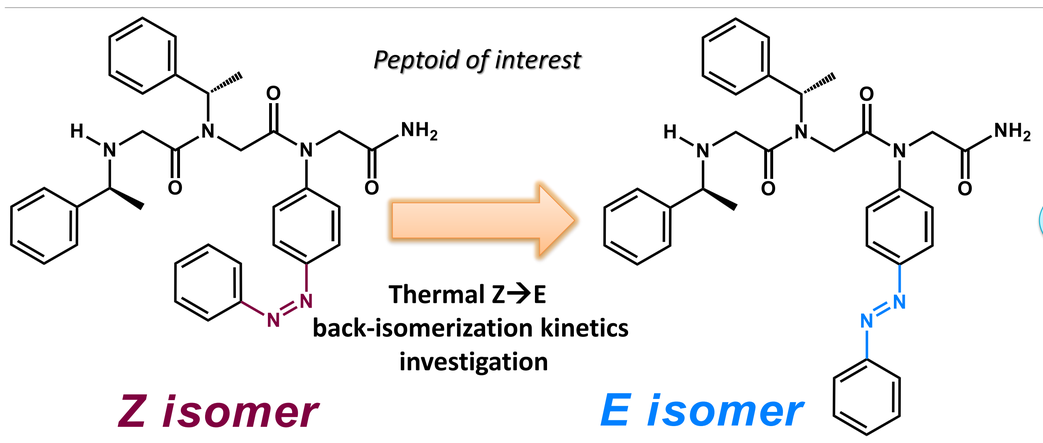



*Figure 3. Primary structure of a peptoid. Example of helical secondary structure with (S)-1-phenylethyl side chain [5].*




## Goal of the study

Key MOST property determination: $E_a$

***In solution:*** **Liquid Chromatography coupled to Mass Spectrometry**
*Waters QToF Premier*

**Comparison**

***Gas phase:*** **Tandem ion mobility spectrometry**
*Original instrument*

ESI | 1st Drift Tube | Ion Trap (T,P,t) | 2nd Drift Tube | MS

Z/E separation and Z selection — Storage and thermal back-isomerization — Second Z/E separation

## Activation barrier in solution

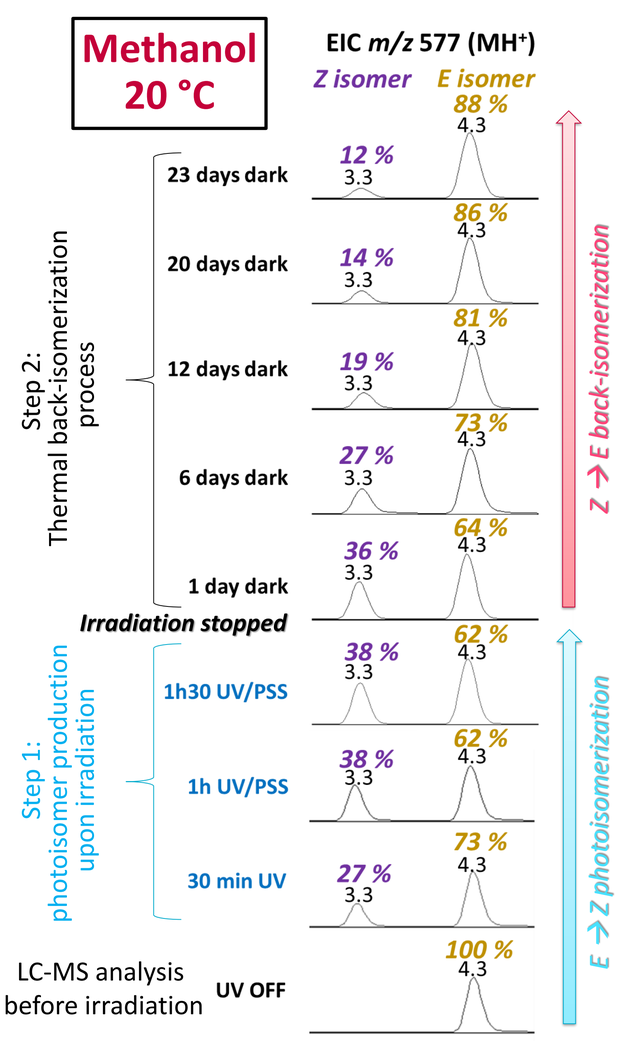



*Figure 4. HPLC-MS (ESI(+)) analyses before irradiation, during irradiation and during thermal relaxation of our azobenzene-containing peptoid.*

**Plotting Z content vs storage time**

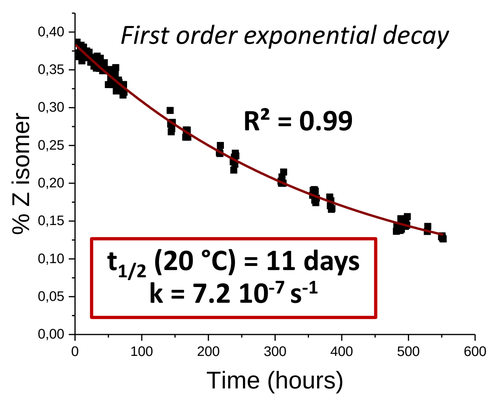



*Figure 5. Peptoid thermal retro-isomerization kinetics at 20 °C followed by HPLC-MS.*

***Experiments at different temperatures***

**Arrhenius plot**

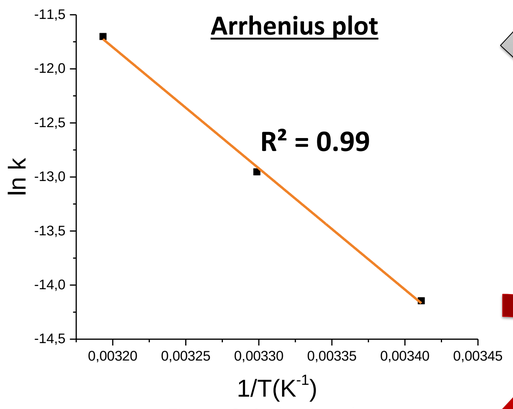



*Figure 6. Arrhenius plot giving access to activation energy.*

$E_a$ = 93 kJ.mol$^{-1}$ in solution (MeOH)

## Gas-phase activation barrier

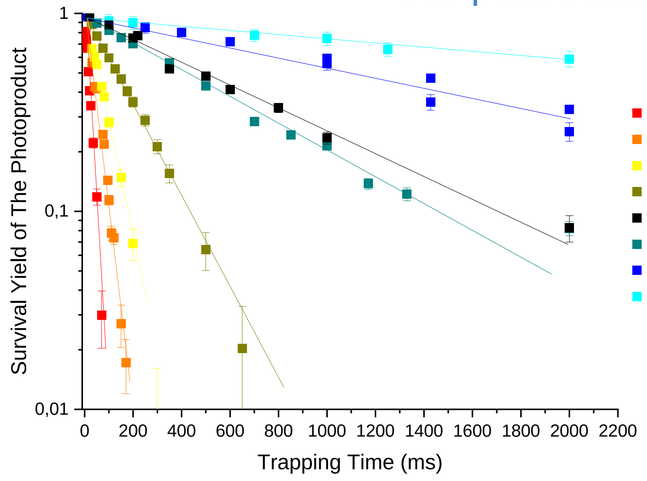



*Figure 7. Gas-phase kinetics at different temperatures using tandem IMS.*

Ion Trap (T,P,t)

*Temperature and Z isomer storage time control*

*Gas-phase thermal back-isomerization kinetics at different temperatures*

**Eyring's plot**

*Give access to kinetics parameters*

$E_a$ = 111 kJ.mol$^{-1}$ in gas phase

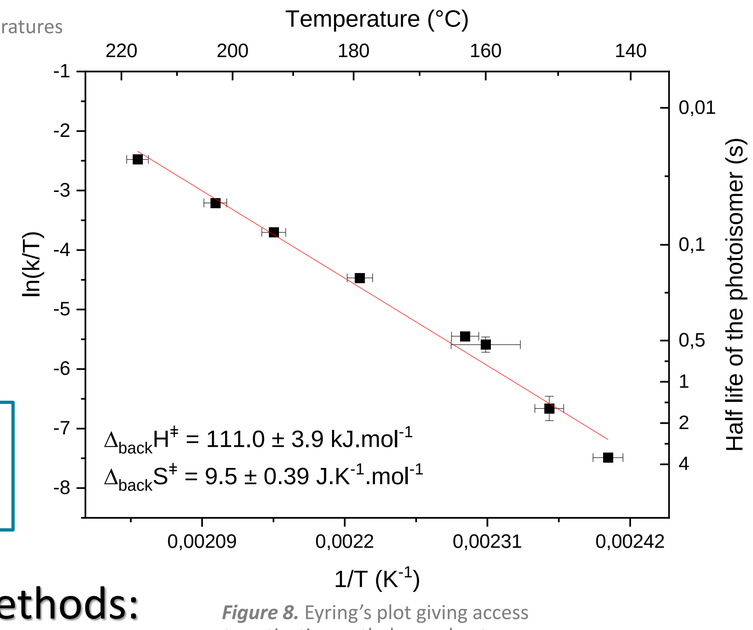



*Figure 8. Eyring's plot giving access to activation enthalpy and entropy for thermal back-isomerization process.*

**Difference between the two methods: effects of solvation and/or ionization ?**

## LC-MS method: pros and cons

**+**
- Efficient and reliable method
- Kinetics measurements for each isomer
- MOST properties in real conditions (molecules in solution)

**−**
- Time (weeks) and solvent-consuming
- Temperature range accessible limited by solvent volatility

## Tandem IMS method: pros and cons

**+**
- Faster than LC-MS method (days)
- Kinetics measurements for each isomer
- Access to high temperatures
- No solvent-dependance

**−**
- Need to study the ionization impact on the isomer structures and on the MOST properties

## Conclusions

In this study, we used peptoid as azobenzene support to store solar energy in the context of MOlecular Solar Thermal systems (MOST). A key parameter for these systems is the activation barrier that determines the storage time of the energy-containing photoisomer. We used two MS-based methods to measure the activation barrier of an azobenzene-containing peptoid both in solution (LC-MS) and in the gas phase (tandem IMS). Values obtained by these two methods are slightly different, probably due to the impact of ionization on the structure of both isomers. This difference will be investigated, in particular with theoretical modelling methods.

## Acknowledgements

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## References

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