Photosensitive macrocyclic peptoids for the chemical storage of solar energy

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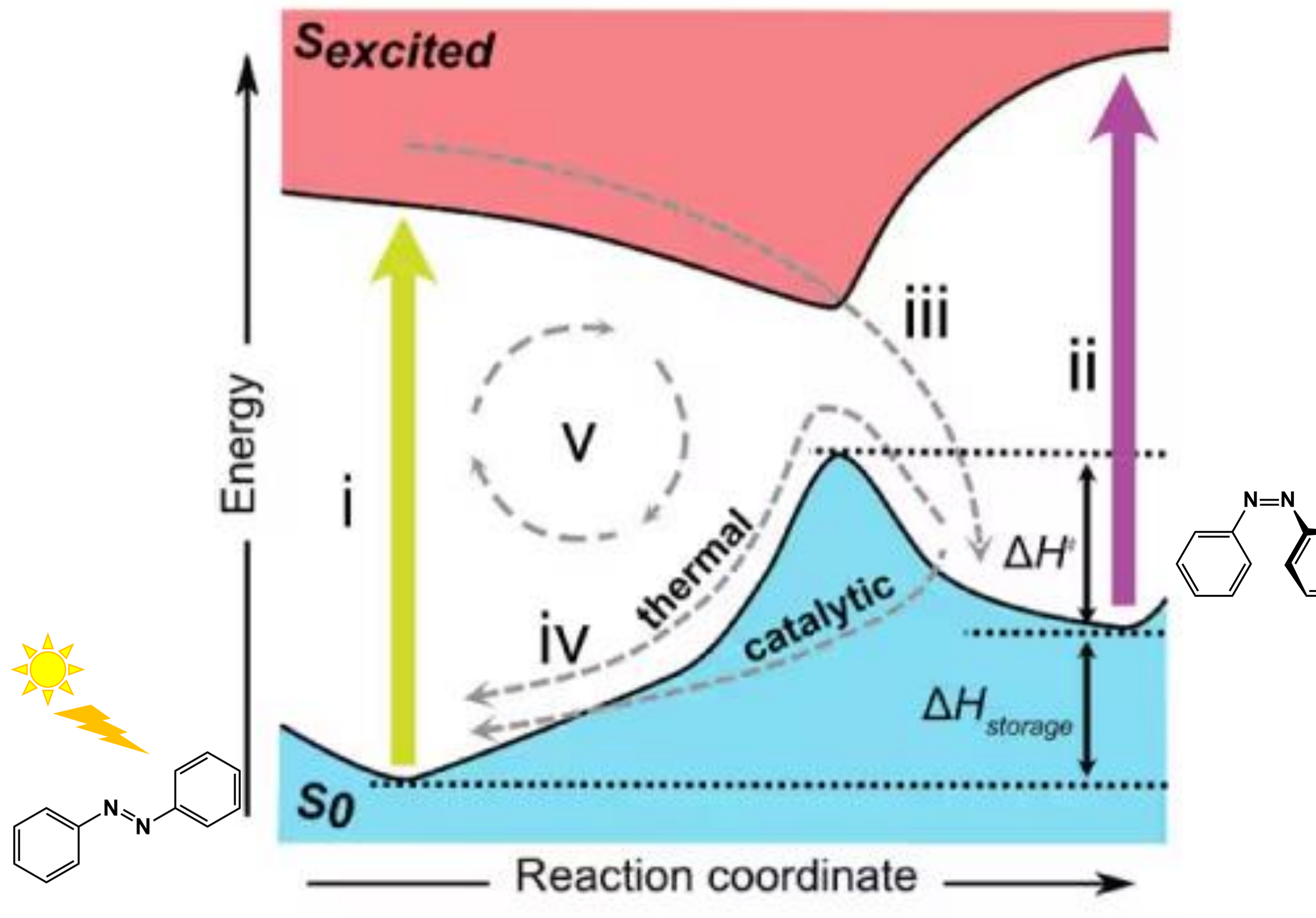


Figure 1. Working principle of MOST system: the azobenzene case: i) stable isomer absorbs sunlight and goes from ground state to excited state, ii) metastable isomer absorbs sunlight and goes from ground state to excited state, iii) deexcitation from the excited state to the metastable isomer ground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

Introduction

The challenge posed by increasing global energy consumption represents a crucial issue for our society. To meet this challenge, harnessing and storing solar energy, an almost limitless resource, has become the focus of increasingly advanced research [1]. One strategy for storing solar energy into chemical bonds is called MOST (MOlecular Solar Thermal systems). The principle involves converting a parent compound into its metastable isomer when it absorbs solar energy, thereby storing the energy as a photoisomer for a certain time. This energy can then be recovered as heat during the back-isomerization [1]. The azobenzene (E/Z) couple appears very promising as a MOST candidate, but it still needs to be optimized for the development of a viable MOST system, especially because of its low storage enthalpy and short half-life [2].

Improving Azobenzene MOST Properties: Incorporation into a Macromolecule

Pristine Azobenzene

- ΔE= 50 kJ.mol^{-1}
- 2 days < $t_{1/2}$ < 4 days
- λ_{max} = 320 nm
- Photostationary state

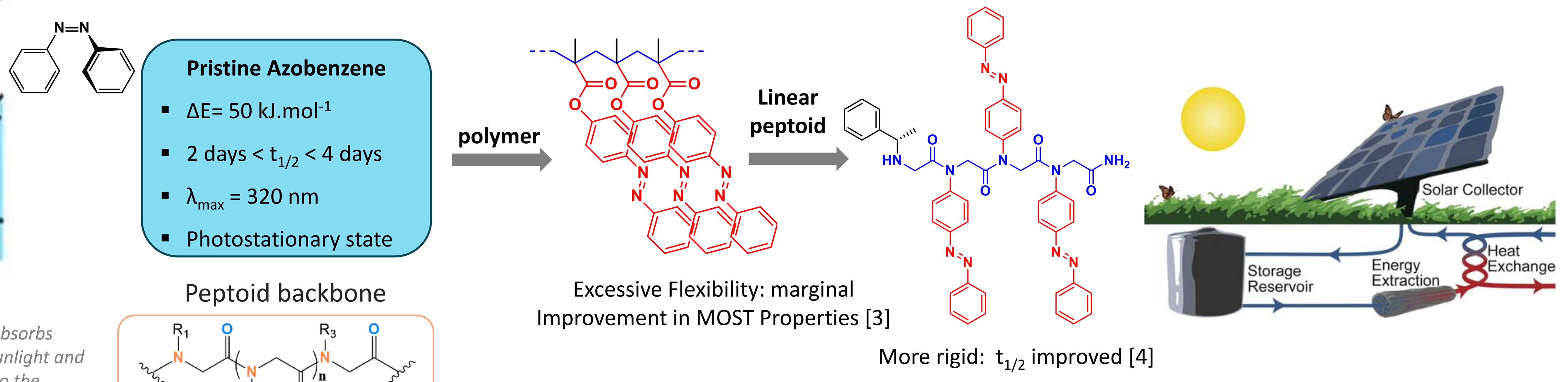
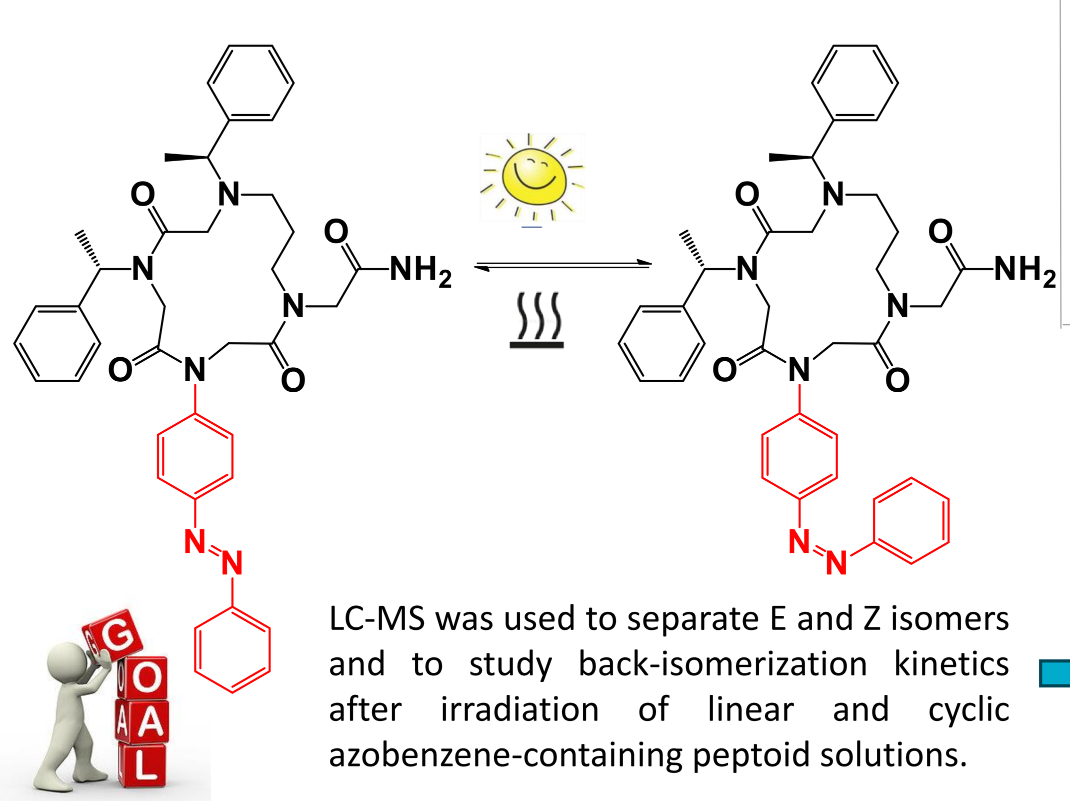


Figure 2. Strategies for improving the MOST properties of azobenzenes.

Experimental pathway

- Linear peptoids synthesis
- Cyclization optimization
- Structural characterization (LC-IMS-MS)
- Back-isomerization kinetics study

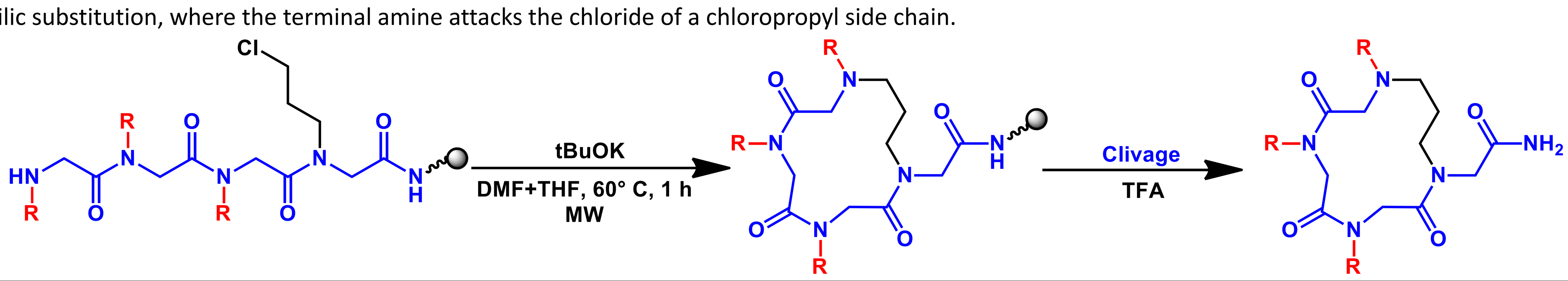


LC-MS was used to separate E and Z isomers and to study back-isomerization kinetics after irradiation of linear and cyclic azobenzene-containing peptoid solutions.

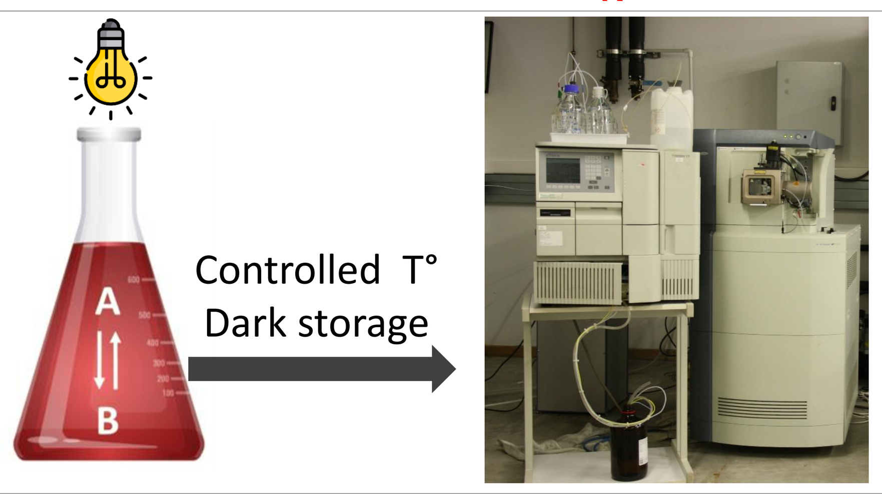
Peptoid cyclization: a promising solution?

The aim of this work is to develop azobenzene-containing cyclic peptoids as promising candidates for MOST energy storage systems. We hypothesize that the interplay between the stereoisomerism of the amide bonds in the peptoid backbone and the conformational constraints imposed by cyclization will significantly influence the relative stabilities of the azobenzene stereoisomers and their back-isomerization kinetics. This approach should produce substantial differences in terms of energy storage capacity (ΔH) and storage time ($t_{1/2}$) compared to linear analogues.

From a synthetic perspective, after creating the desired sequence, cyclization occurs on the resin. This process begins with the linear precursor peptoid and involves a nucleophilic substitution, where the terminal amine attacks the chloride of a chloropropyl side chain.



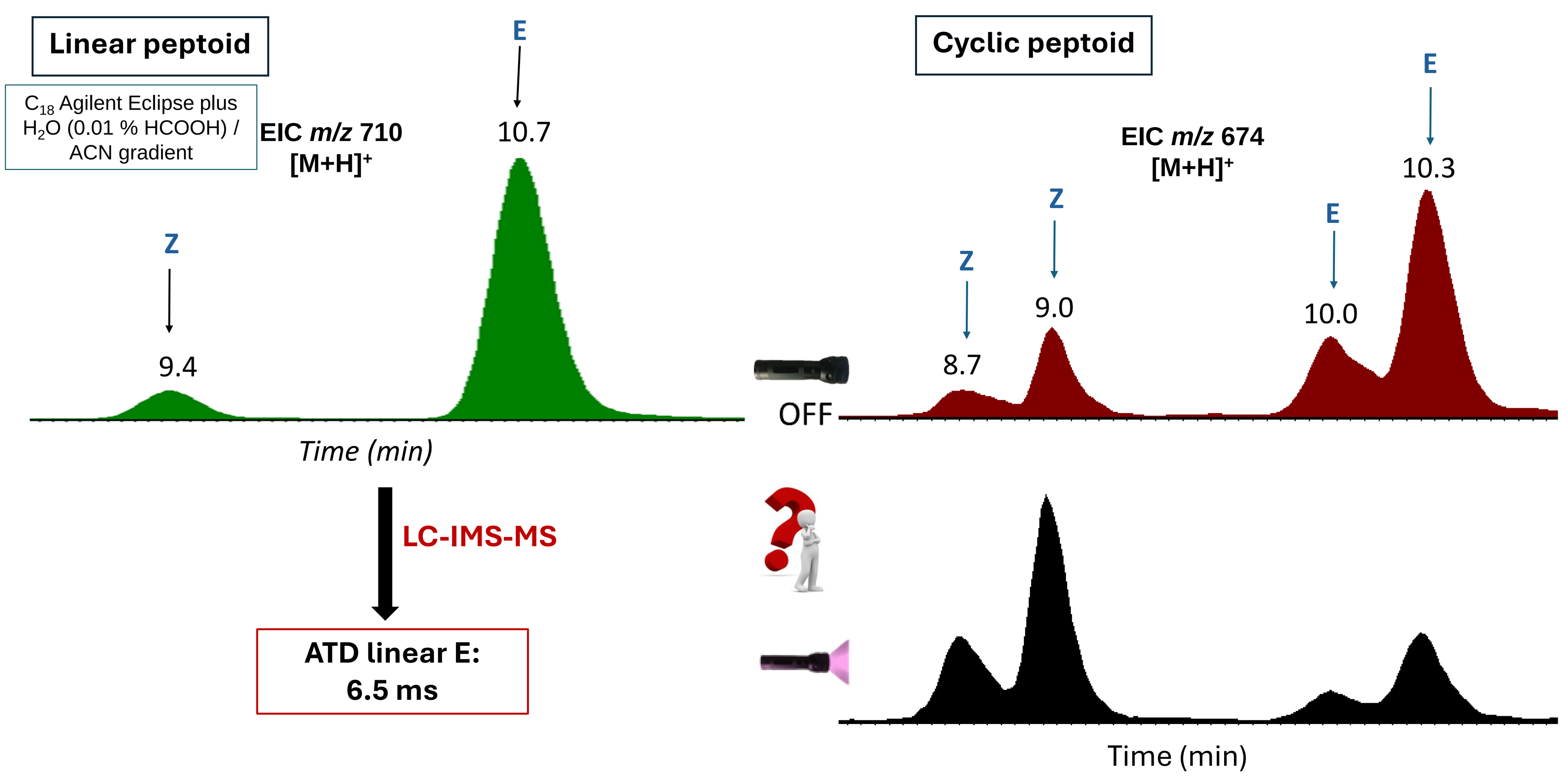
Back-isomerization in solution: LC-MS investigation

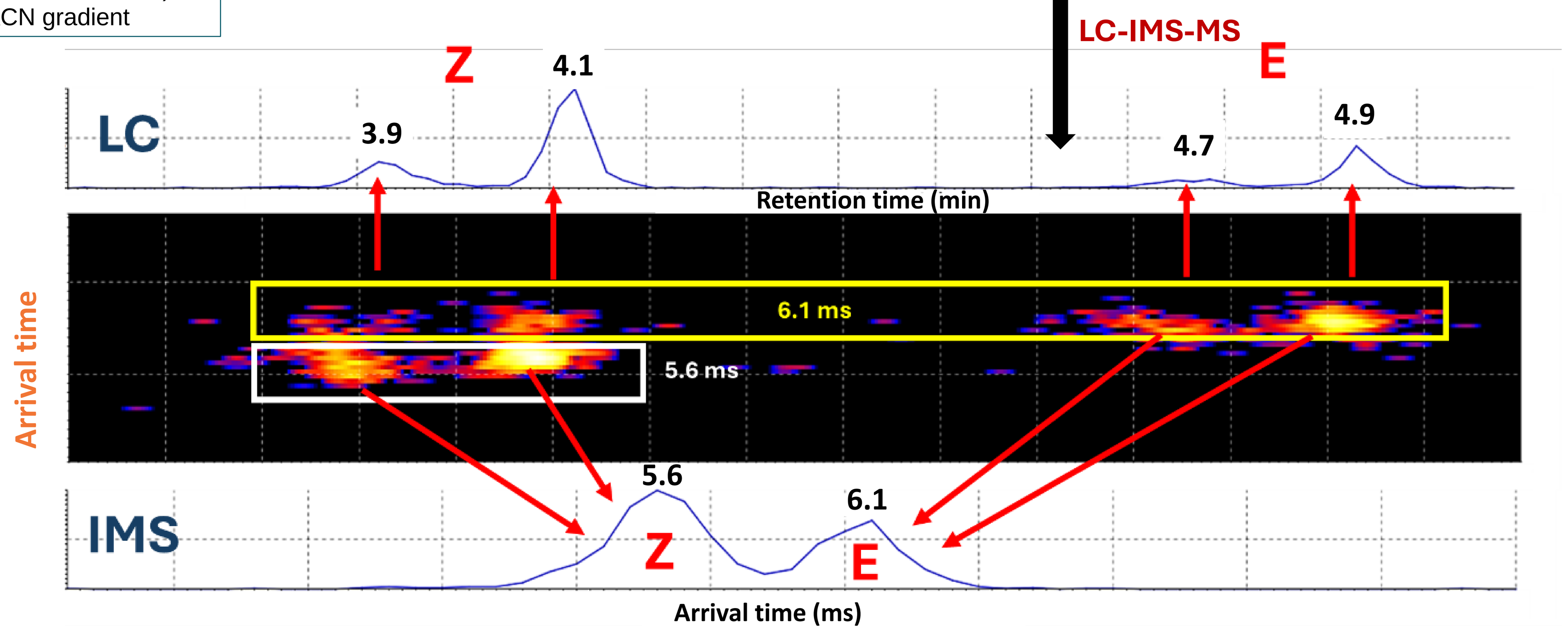


$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT};\ t_{1/2} = \frac{\ln 2}{k}$$

E / Z ratio evolution

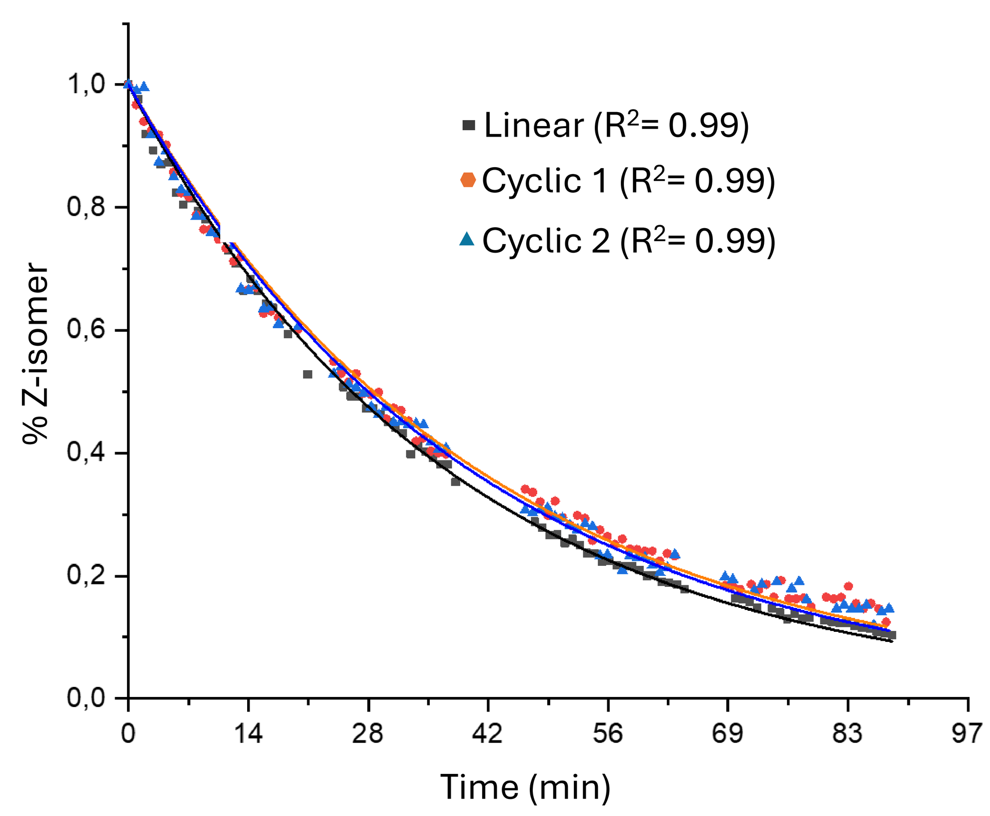
Kinetics parameters determination



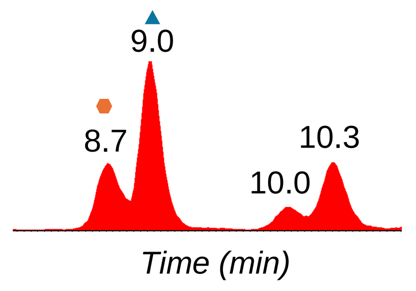


Two pairs of cyclic peptoids observed, resulting from the cyclization reaction (S_N2) stereochemistry

Linear and cyclic azobenzene-containing peptoid solutions were irradiated with a lightningcure Arimed B6 UV lamp (ca. 290 - 350 nm), to induce azobenzene isomerization. Back-isomerization kinetics were studied by liquid chromatography (Waters Alliance 2655) coupled to mass spectrometry (Waters QToF-US, ESI) in MeOH at **40°C**.



Thermal back-isomerization of linear and cyclic peptoids at 40 °C in MeOH.

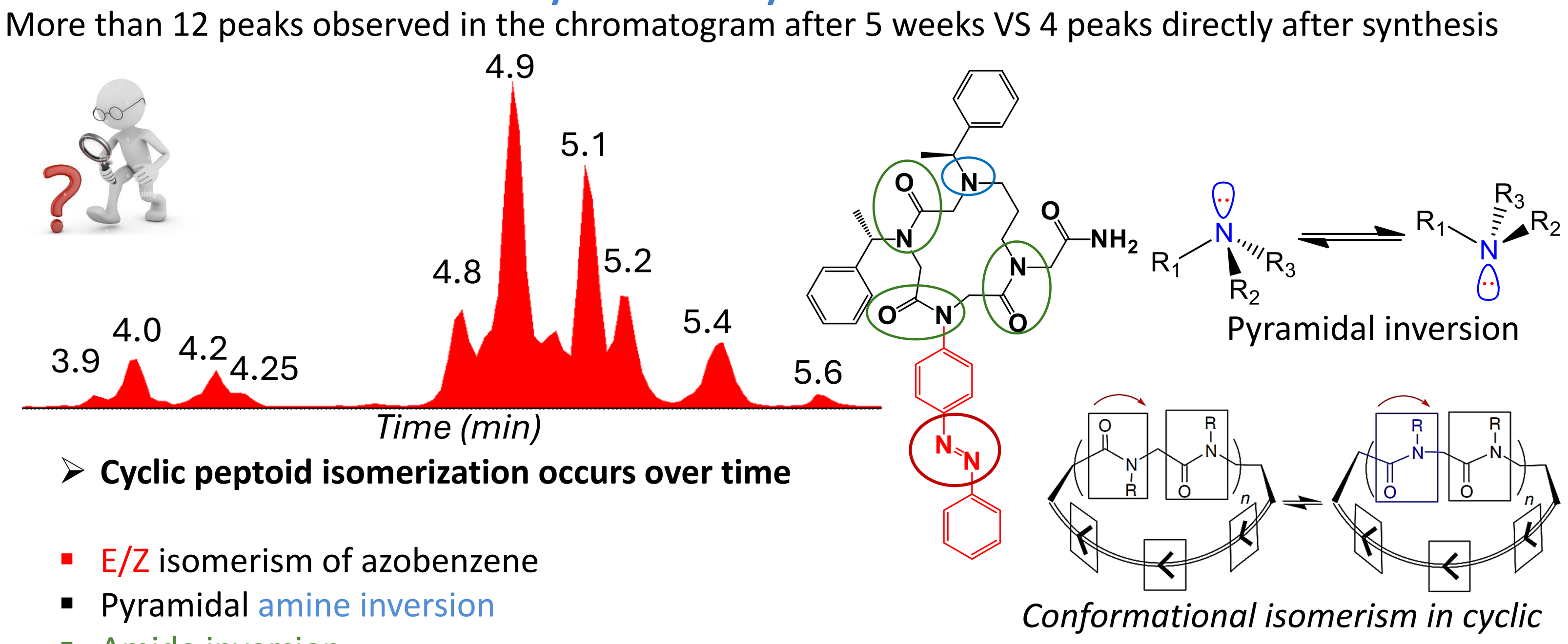


Cyclization increases half-life by around **2 h**

	k ($10^{-6}s^{-1}$)	$t_{1/2}$ (h)
Linear	7.44 ± 0.04	25.87 ± 0.14
Cyclic 1	6.78 ± 0.05	28.38 ± 0.22
Cyclic 2	6.94 ± 0.06	27.74 ± 0.24

Dynamic system?

More than 12 peaks observed in the chromatogram after 5 weeks VS 4 peaks directly after synthesis



- **Cyclic peptoid isomerization occurs over time**

- E/Z isomerism of azobenzene
- Pyramidal amine inversion
- Amide inversion

Conformational isomerism in cyclic peptoids: amide bond inversion [5].

Conclusions

This work, which combines synthesis, LC-MS, and LC-IMS-MS analyses, demonstrates that it is possible to improve the half-life of the metastable azobenzene isomer by grafting it onto cyclic peptoids. However, we are facing a dynamic system, as the number of peaks in the chromatogram increased after storing the sample at room temperature for five weeks. Consequently, the next step will be to understand the conformational dynamics before assessing the other MOST properties.

Acknowledgments

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References

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