Phenylazothiazole photoswitches on macromolecules for solar energy storage : photoisomerization and thermal back isomerization kinetics by MS

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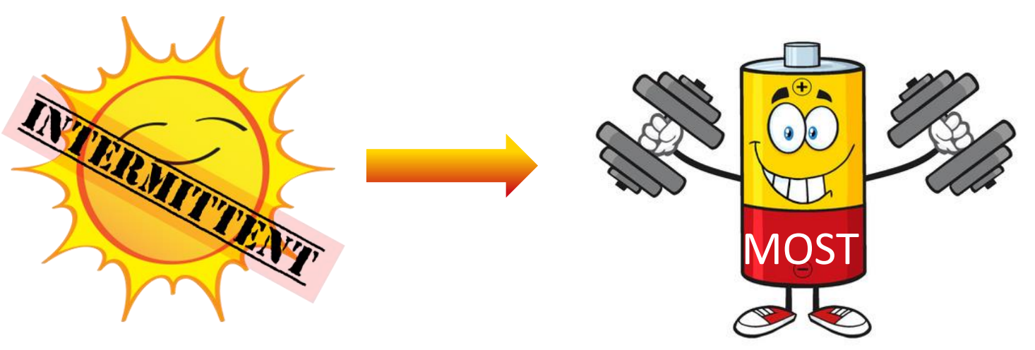
Energy Challenges : a matter of storage?

Sun as renewable energy source



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].

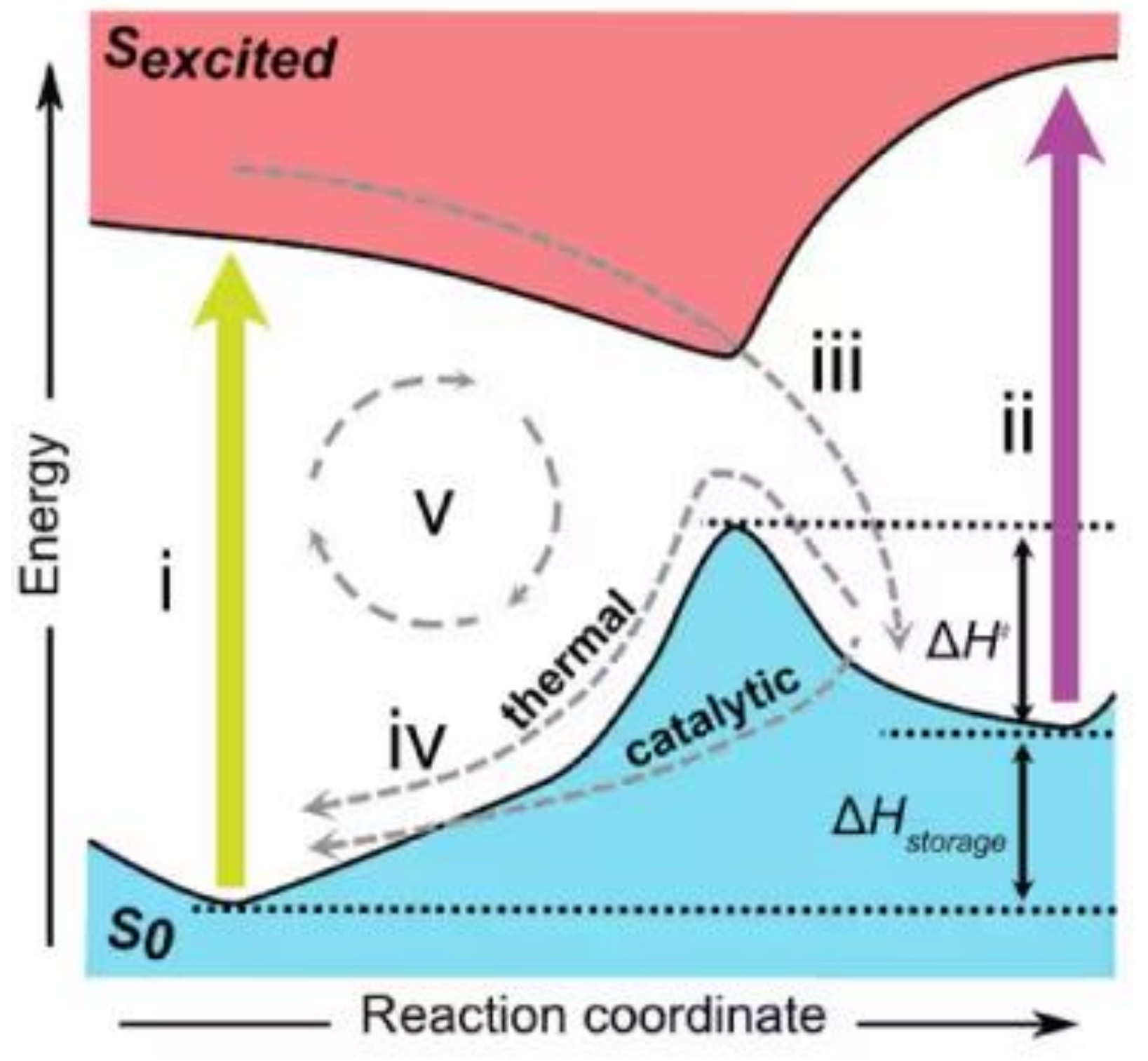


Figure 1. *Working principle of MOST system: i) stable isomer absorbs sunlight and goes from ground state to excited state, ii) metastable isomer absorbs sunlight and goes from ground state to excited state, iii) deexcitation from the excited state to the metastable isomer ground state, iv) thermal or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

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.

Improving azobenzene MOST properties

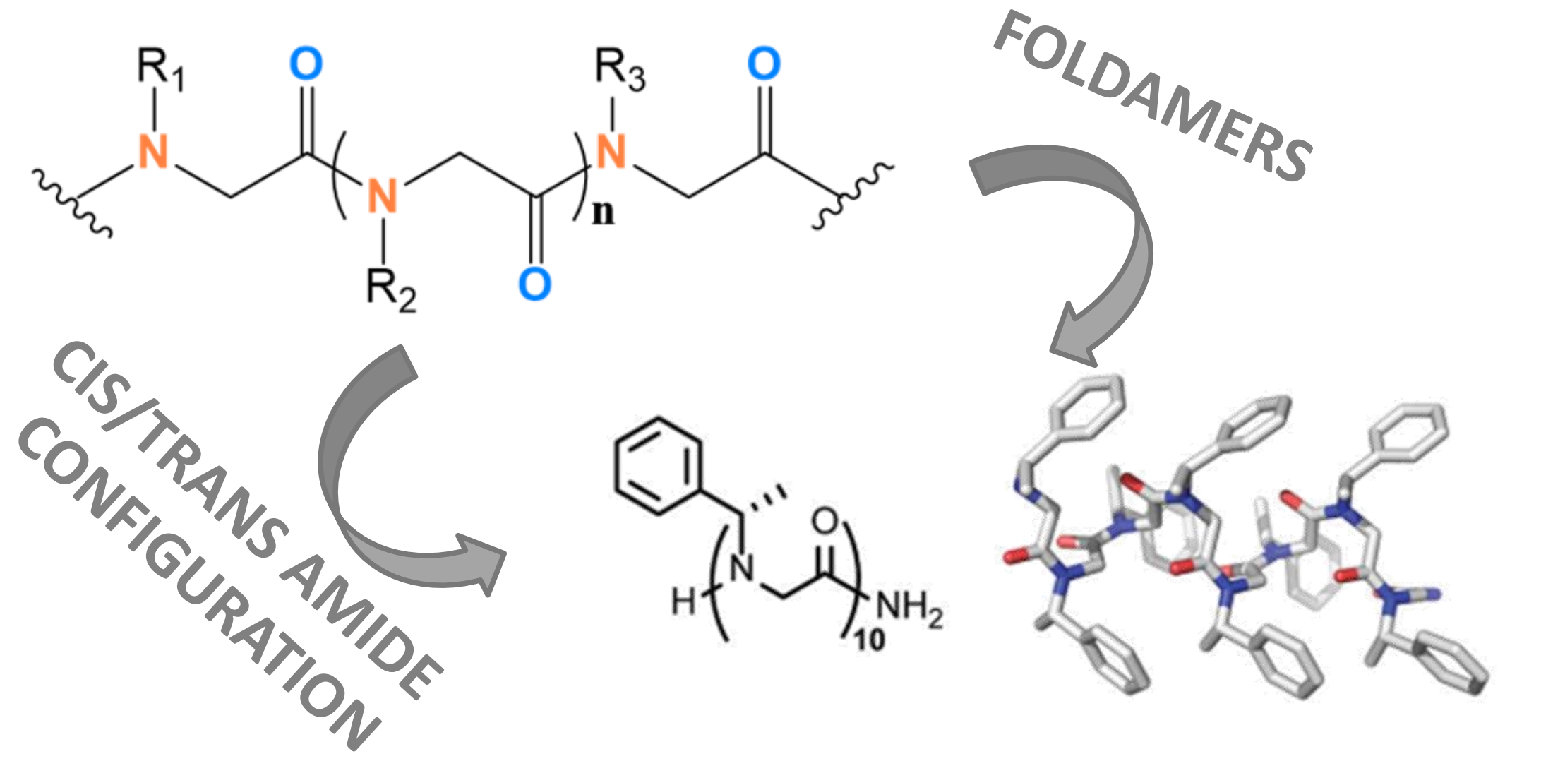


Figure 2. *Primary structure of a peptoid.*
Exemple of helical secondary structure with (S)-1-phenylethyl side chain [8].

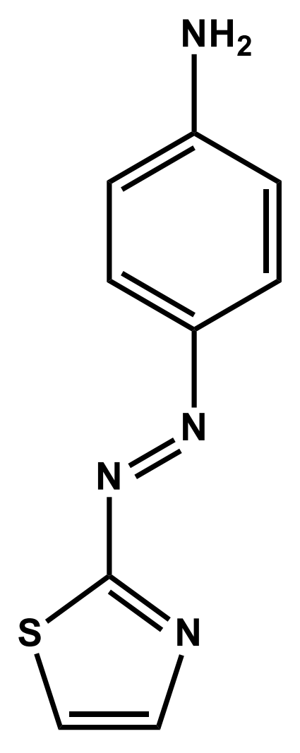
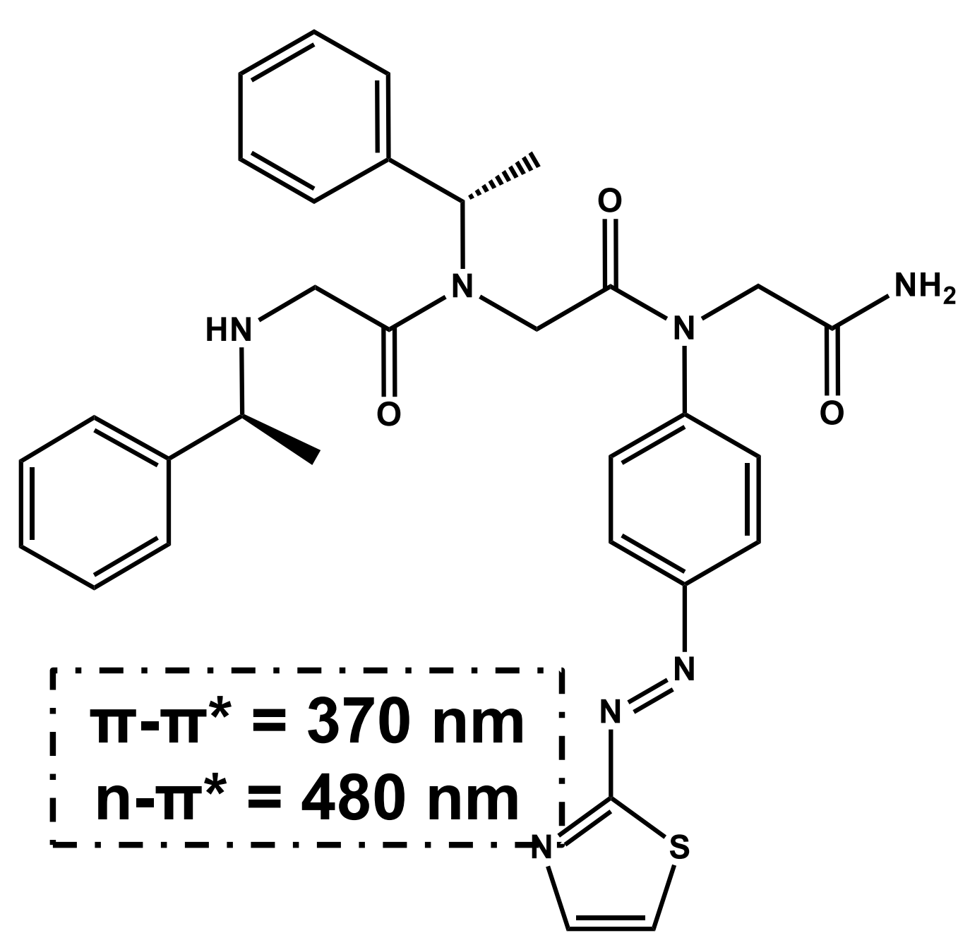


Figure 3. *(E)-4-(thiazol-2-yldiazenyl) aniline [5].*

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].

Peptoid of interest

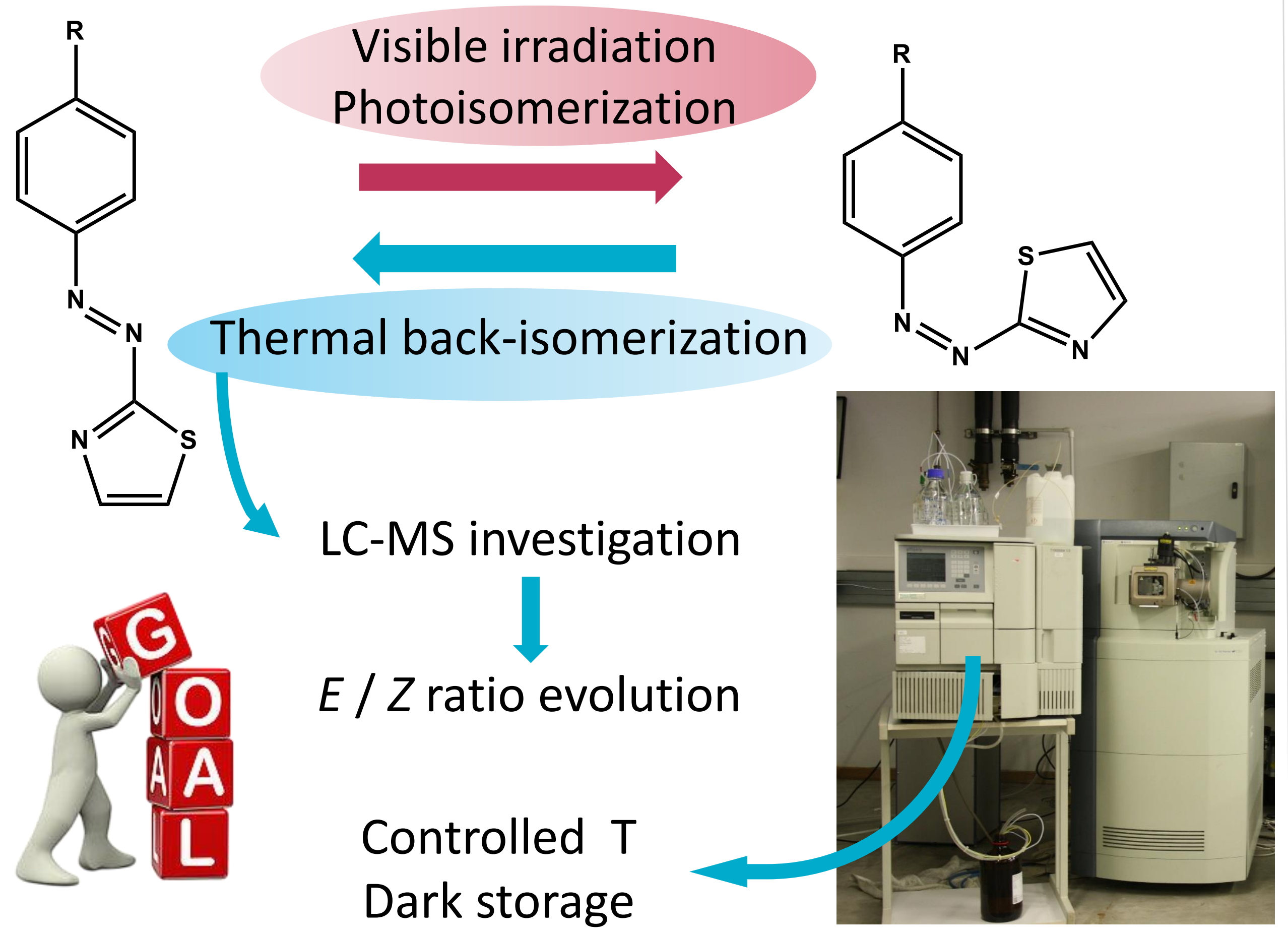


π-π* = 370 nm
n-π* = 480 nm

Figure 4. Structure of the NspeNspeN2tz peptoid with spectroscopic transition

Anchoring AB photoswitches on a peptoid chain is performed using an on-resin step-by-step synthetic procedure allowing to incorporate different side chains at selected positions. Two different residues are incorporated in our photoactive peptoids; i.e., (*S*)-phenylethylamine (N*spe*) and (E)-4-(thiazol-2-yldiazenyl) aniline (N*2tz*). NspeNspeN2tz, was successfully synthetized, purified and primary structure was confirmed based on MS/MS analysis.

Methods: LC-MS approach



Visible irradiation
Photoisomerization

Thermal back-isomerization

LC-MS investigation

E / *Z* ratio evolution

Controlled T
Dark storage

Back-isomerization Monitoring with LC-MS*

In MeOH at 293 K

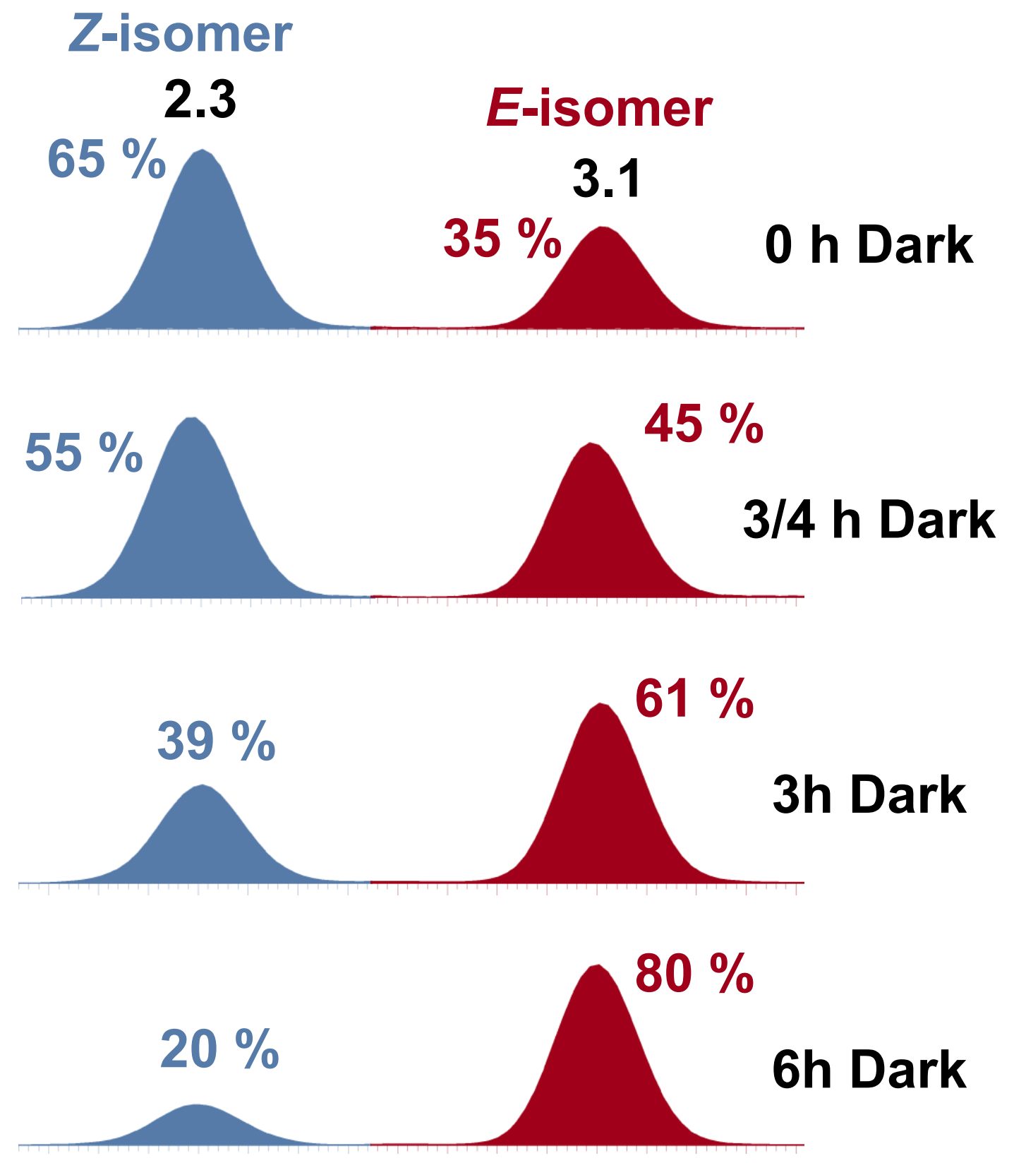


Figure 4. *LC-MS analyses [EIC chromatograms of the $[M+H]^+$ ions at m/z 584] of the thermal back-isomerization of NspeNspeN2tz in MeOH stored in the dark chamber of the LC autosampler at 293 K.*

**LC-MS: Alliance 2695 HPLC (Waters, UK), equipped with an Agilent Eclipse Plus C18 column (4.6×100 mm; 3.5 µm particle size) coupled to Waters QToF Premier mass spectrometer.*

What about
Other Solvent

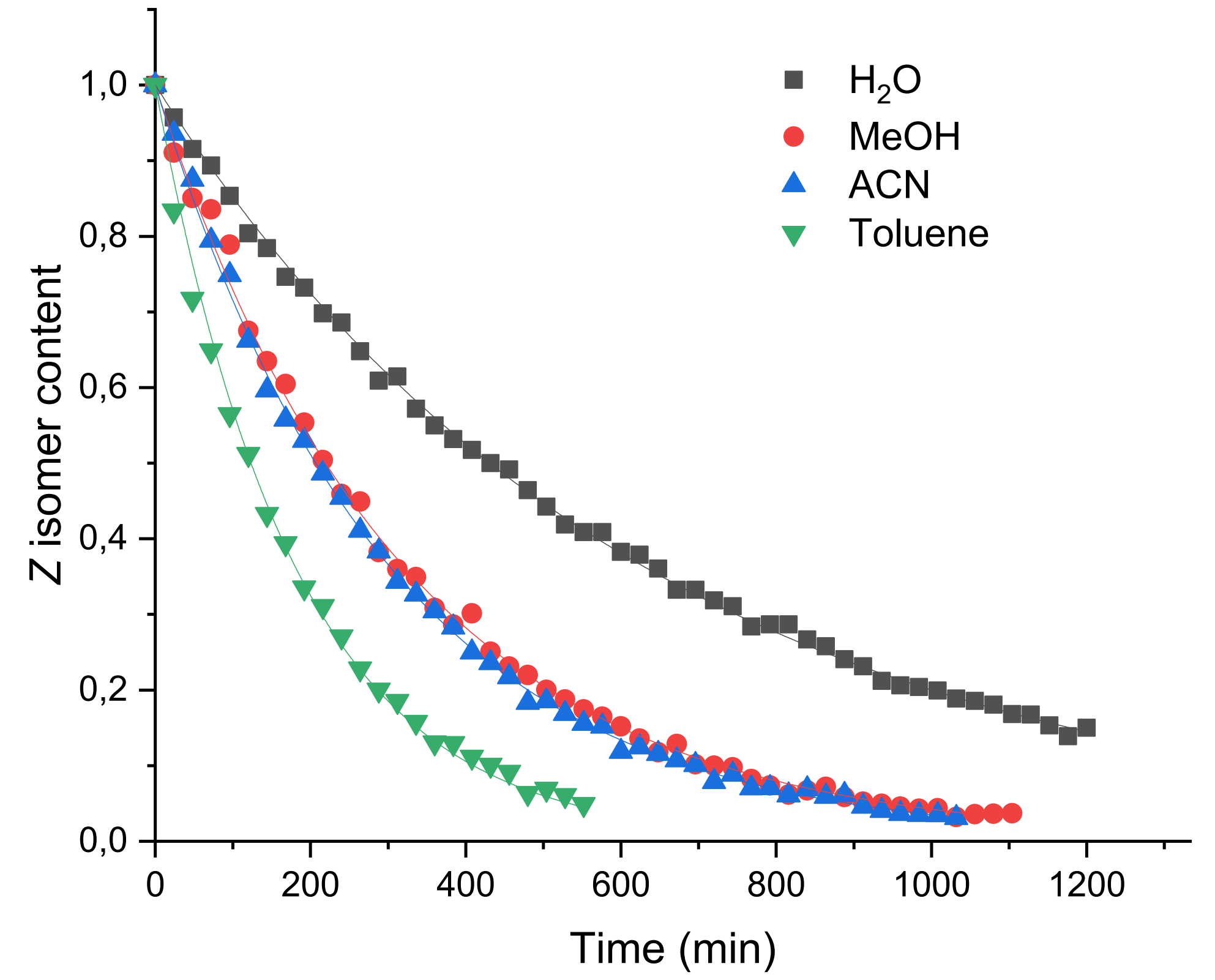


Figure 5. *Thermal back-isomerization of NspeNthiaNspe and NspeNspeNthia at 293 K in H_2O, ACN, MeOH and toluene.*

Solvent	k_{avg} (10^{-5} s^{-1})	$t_{1/2}$ (h)
H_2O	2.73 ± 0.05	7.04 ± 0.14
ACN	5.25 ± 0.33	3.68 ± 0.24
MeOH	5.30 ± 0.03	3.63 ± 0.03
Toluene	8.78 ± 0.58	2.20 ± 0.14

Half-life time increase with polarity and proticity

Mechanism of back-isomerization?

Kinetics parameter in different solvents

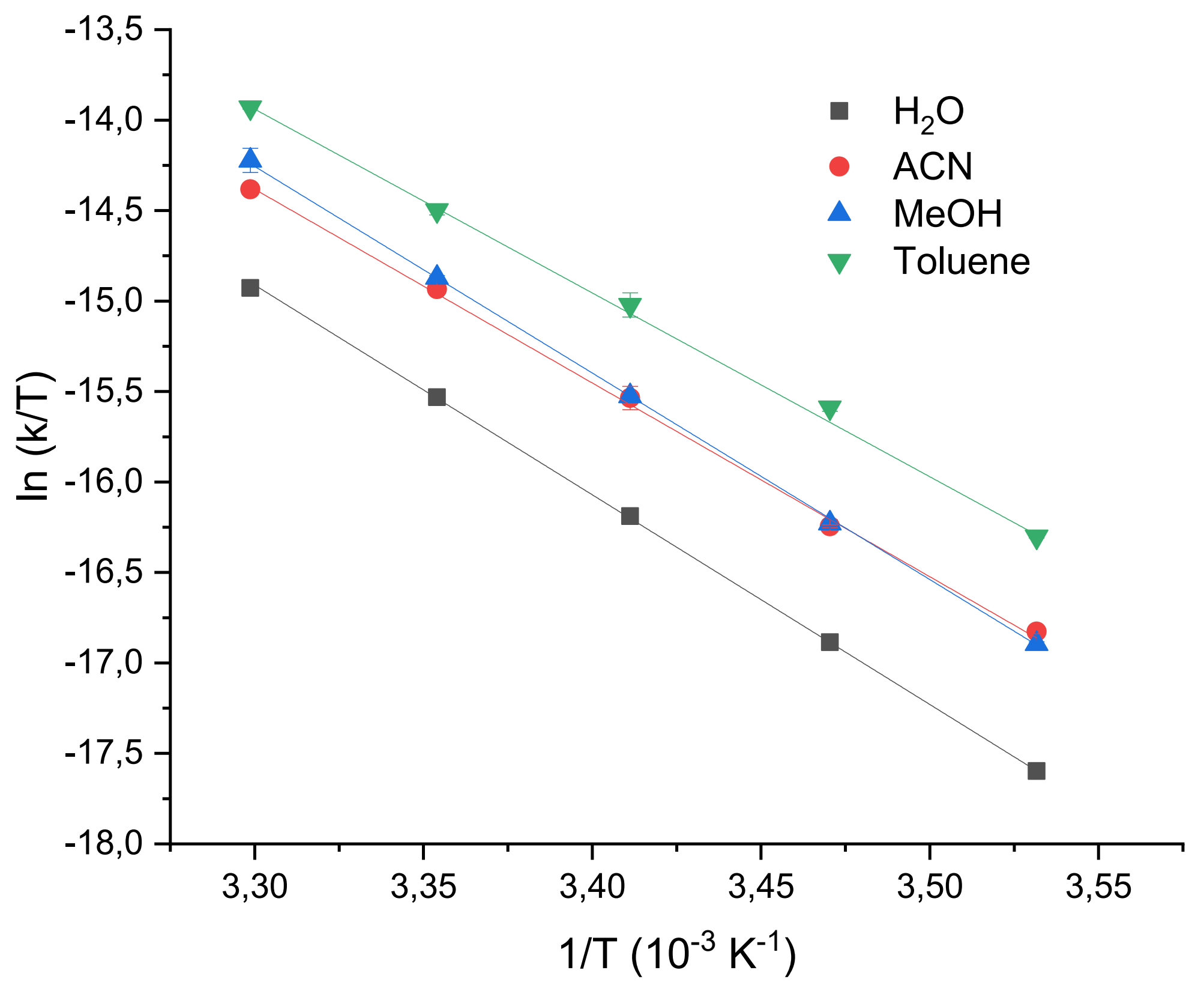


Figure 6. *Eyring plot for the NspeNspeN2tz thermal back-isomerization in H_2O, ACN, MeOH and toluene.*

■ H_2O

$\Delta H^‡ = 96.35 \pm 0.34$ kJ.mol^{-1}
$\Delta S^‡ = -3.6 \pm 1.2$ J.mol^{-1} K^{-1}
$\Delta G^‡$ (293 K) = 97.4 ± 0.7 kJ.mol^{-1}

● ACN

$\Delta H^‡ = 89.02 \pm 1.65$ kJ.mol^{-1}
$\Delta S^‡ = -23.4 \pm 5.6$ J.mol^{-1} K^{-1}
$\Delta G^‡$ (293 K) = 95.86 ± 3.3 kJ.mol^{-1}

▲ MeOH

$\Delta H^‡ = 94.90 \pm 0.63$ kJ.mol^{-1}
$\Delta S^‡ = -2.9 \pm 2.2$ J.mol^{-1} K^{-1}
$\Delta G^‡$ (293 K) = 95.75 ± 1.28 kJ.mol^{-1}

▼ Toluene

$\Delta H^‡ = 84.44 \pm 1.05$ kJ.mol^{-1}
$\Delta S^‡ = -34.8 \pm 3.6$ J.mol^{-1} K^{-1}
$\Delta G^‡$ (293 K) = 94.64 ± 2.1 kJ.mol^{-1}

It appears that the less polar the solvent is, the more negative the entropy becomes

different back-isomerization pathway

Conclusion

Through this study, which combines synthesis and LC-MS characterization, we demonstrate the effectiveness of the LC-MS method for accurately determining the half-life of the Z-isomer in various solvents and at different temperatures. Among the solvents tested, water yielded the longest half-life, suggesting it is particularly suitable for the storage of solar energy. Overall, a trend was observed in which decreasing solvent polarity correlates with a shorter Z-isomer half-life. Furthermore, LC-MS analyses conducted at different temperatures allowed us to determine the kinetic parameters in each solvent. A clear trend emerged: as solvent polarity decreases, the activation entropy becomes more negative. This observation suggests a potential modification of the back-isomerization mechanism, likely driven by environmental factors such as solvent polarity and proticity. The next step in this investigation will involve theoretical modeling in various solvents to better understand how these factors influence the isomerization pathway

References

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Acknowledgments

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