Mass Spectrometry and Photochemical Study of Photoisomerization and Thermal Back-isomerization of Substituted Azobenzenes anchored on Peptoids for the Chemical Storage of Solar Energy

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Energy challenges: a matter of storage?

Sun as renewable energy source

Storage

MOlecular Solar Thermal systems (MOST)
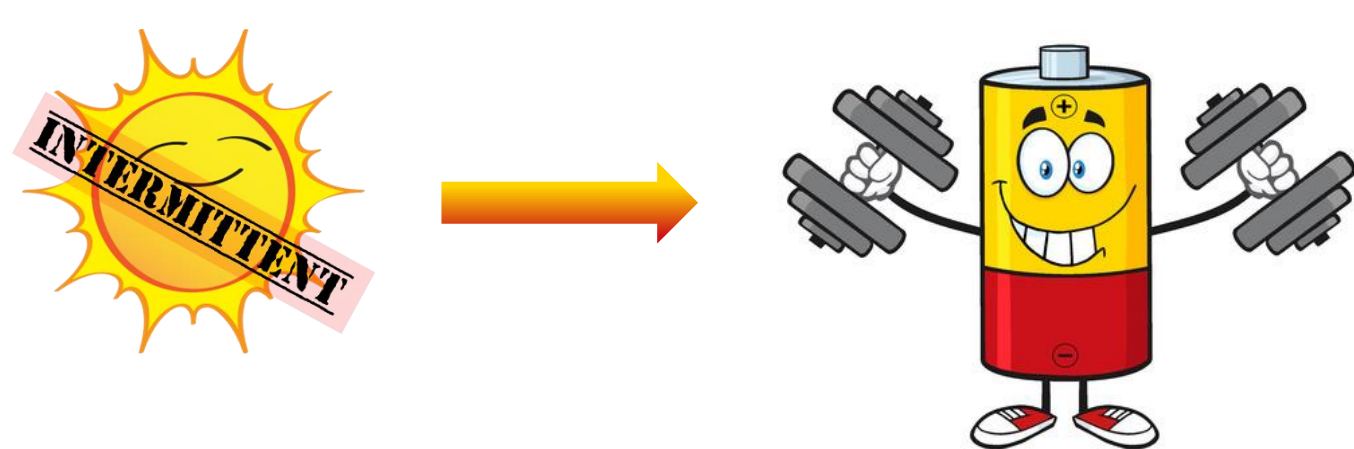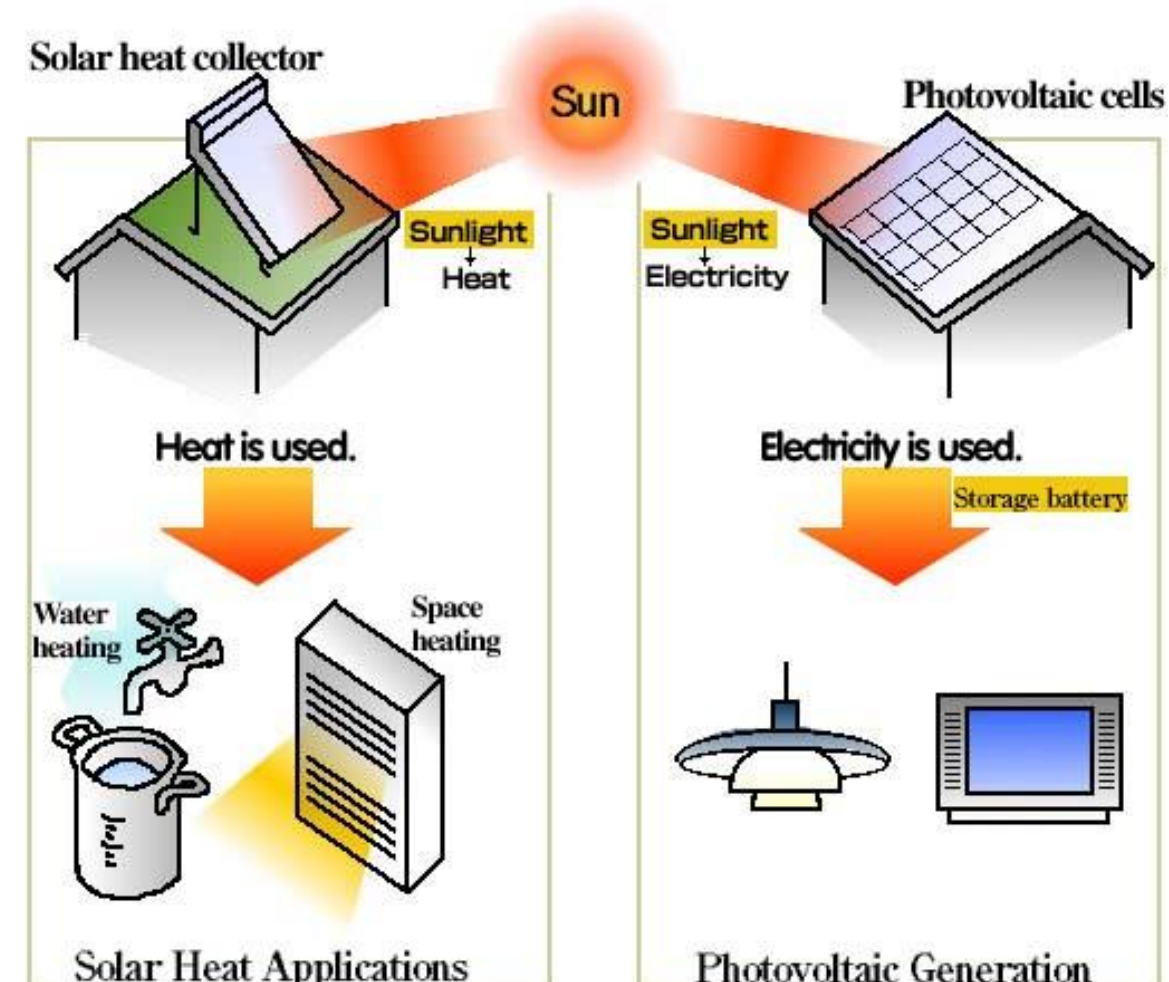
To store solar energy, chemical storage appears to be a promising approach with systems known as MOST [1]. The working principle of those systems is based on iterative closed cycles of photoisomerization and back-isomerization between a parent compound and its metastable isomer (*Figure 1*). Energy is 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].

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.
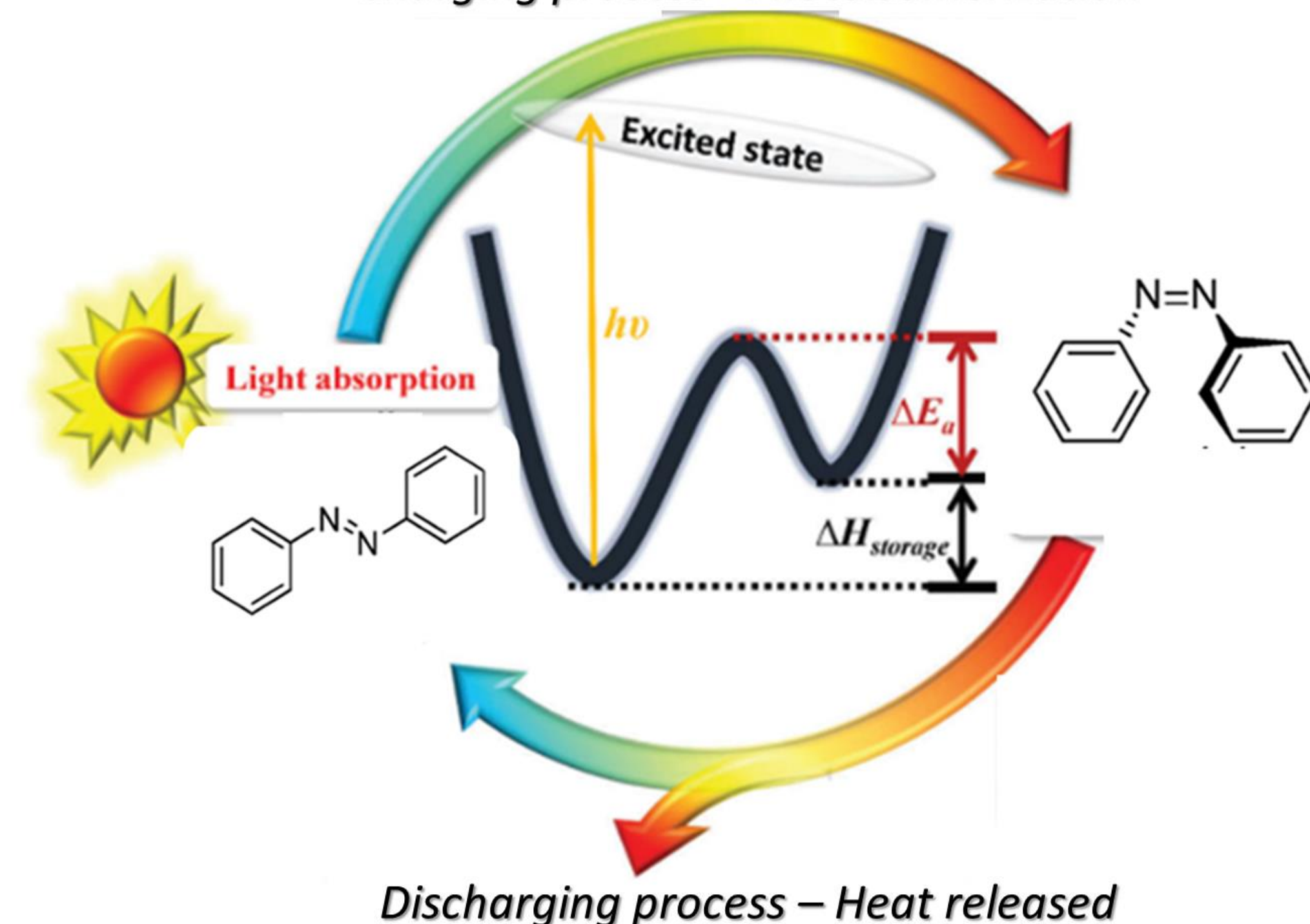

Figure 1. Working principle of a MOST system: the azobenzene case [3].

Improving azobenzene MOST properties: our strategy

Azobenzene properties must be improved. To do so, different strategies have been considered in literature and grafting azobenzenes at selected positions all along a polymer backbone appears to be an elegant way to enhance these properties thanks to cooperative effects between the chromophores [4-5]. Anchoring ABs 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 [6]. To strengthen the inter side-chain interaction, we intend to incorporate H-bond donors and acceptors on the pending chains to create an H-bond network.
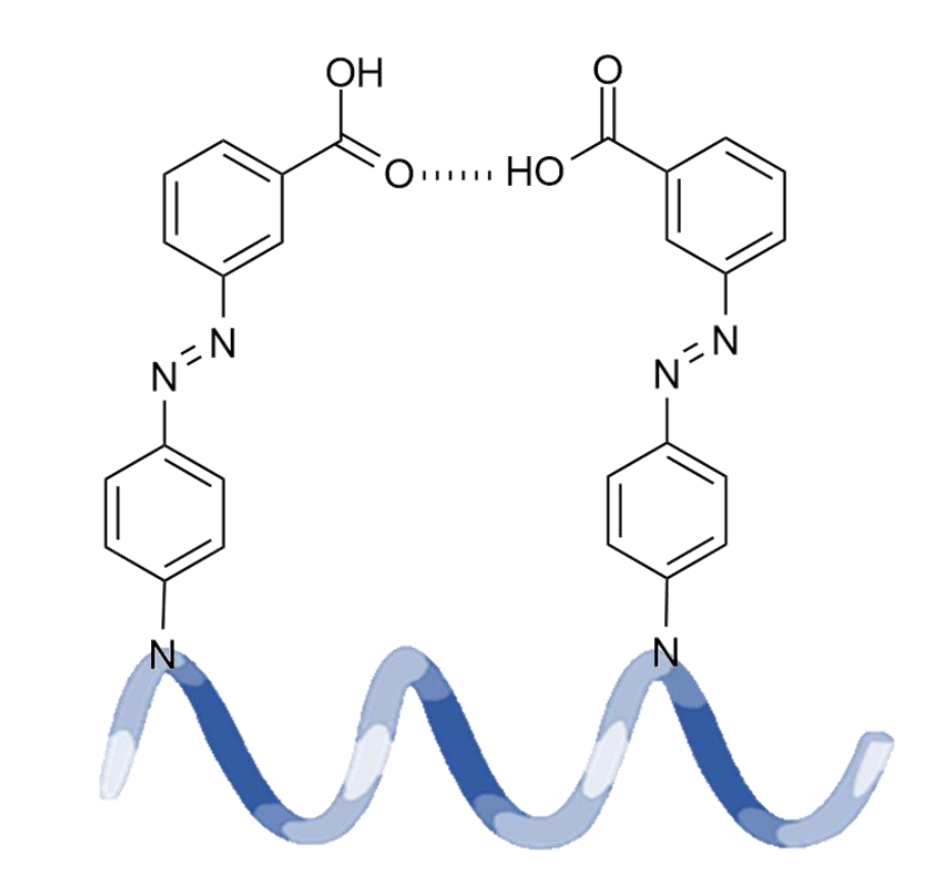

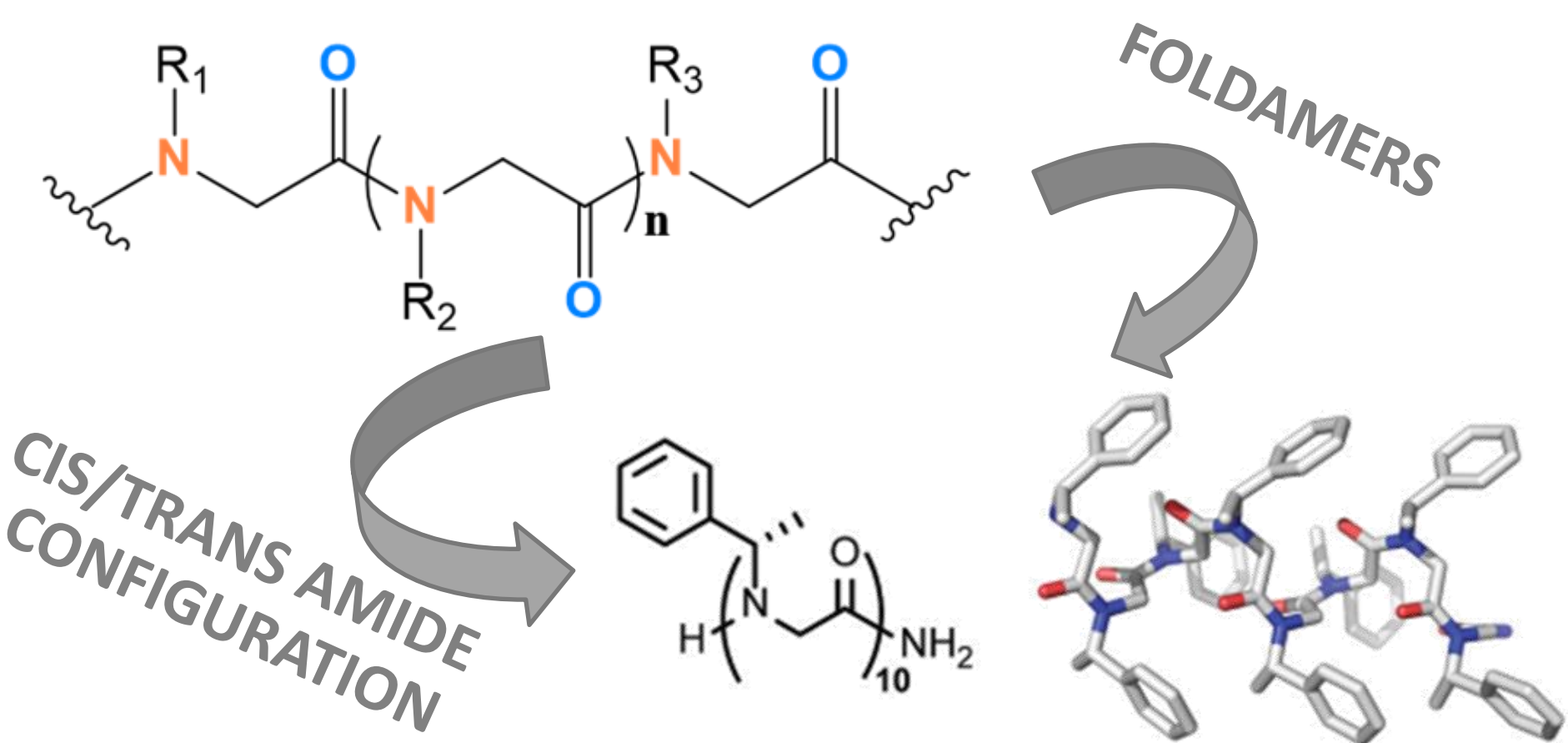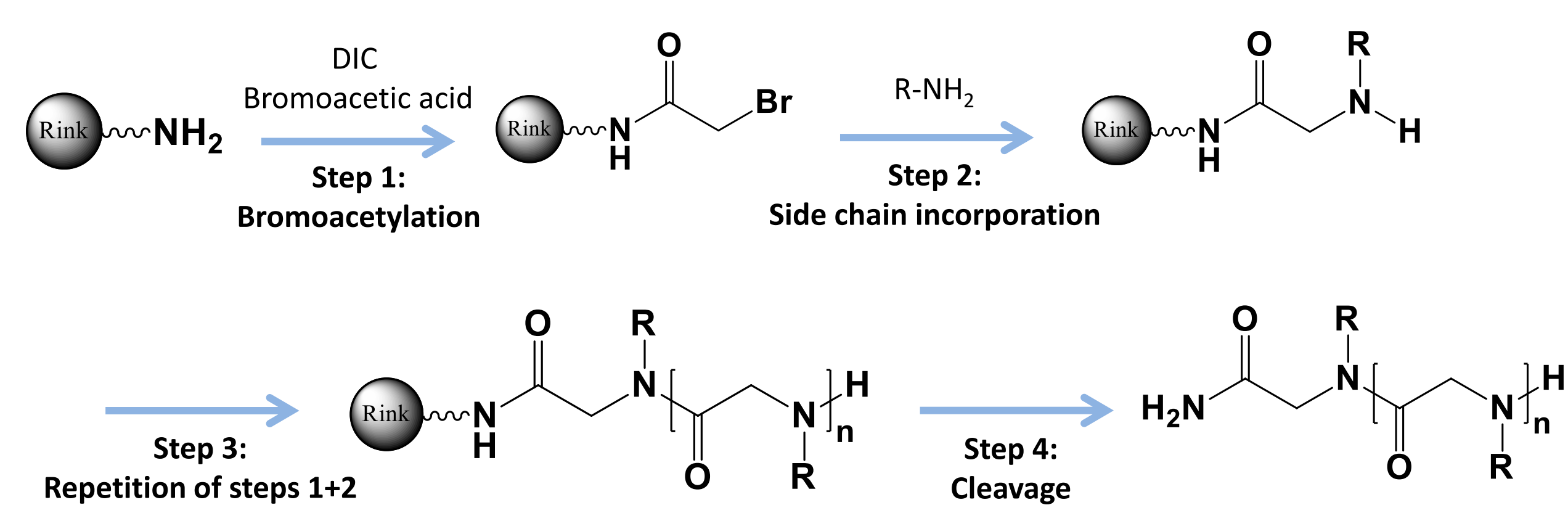*Figure 2. Primary structure of a peptoid.*
Exemple of helical secondary structures with (S)-1-phenylethyl side chain [7].

Figure 3. Inter side-chain H-bond network.

Peptoids of interest: solid support synthesis

Step 1: Bromoacetylation

Step 2: Side chain incorporation

Step 3: Repetition of steps 1+2

Step 4: Cleavage

Peptoid 1 (n=1): N*spe*N*azo*N*spe*
Peptoid 2 (n=2): (N*spe*N*azo*N*spe*)₂

Peptoid 3 (n=1): N*spe*N*azoest*N*spe*
Peptoid 4 (n=2): (N*spe*N*azoest*N*spe*)₂

Spectroscopic analyzes: UV-Vis

UV-Vis spectra were recorded on a Perkin Elmer Lambda 35 UV/Vis spectrophotometer. Solutions (C = 5.10^-5 M) were prepared in the dark in MeOH HPLC grade.
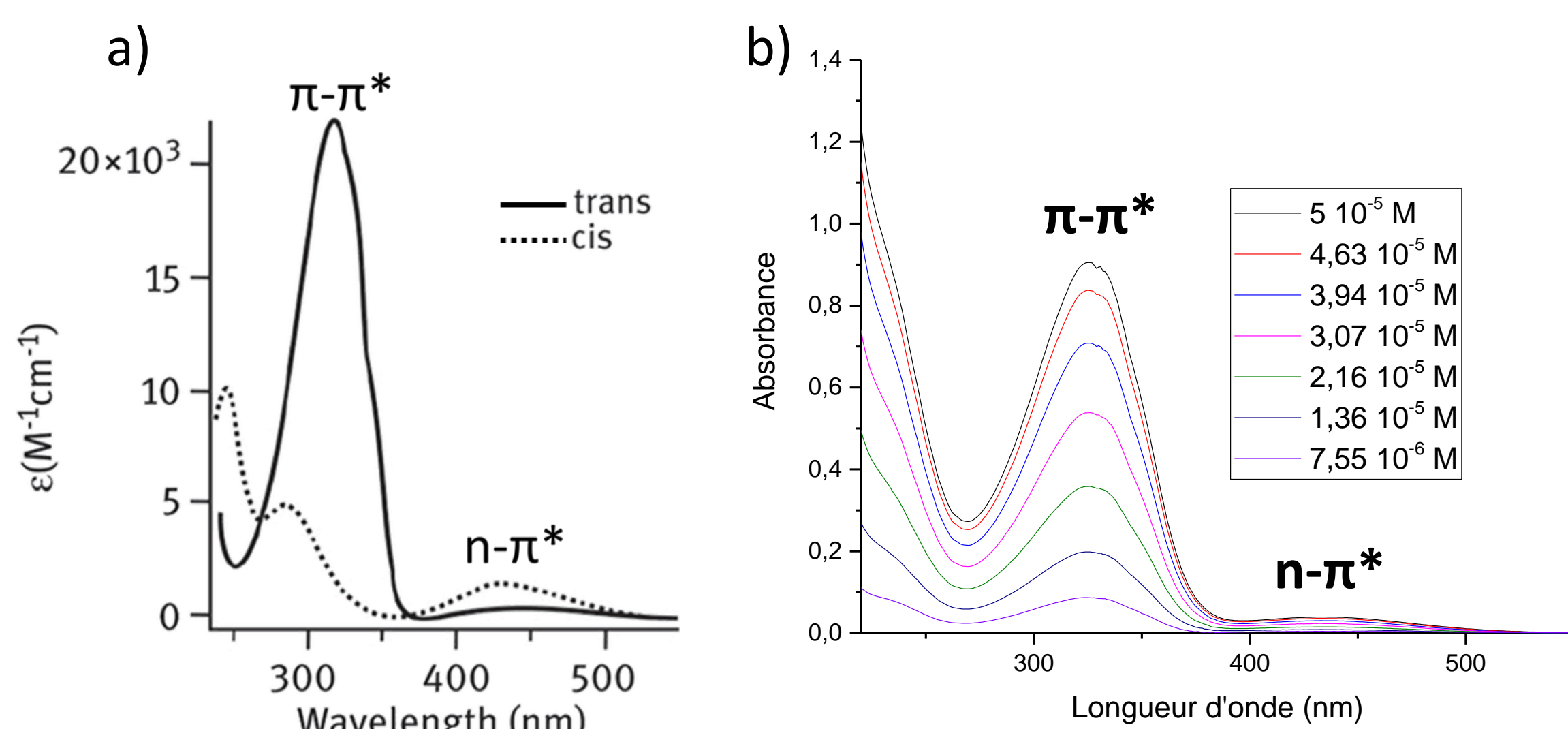

Figure 4. a) UV-Vis spectrum of azobenzene [8]. b) Typical UV-Vis spectra of peptoids.

Molecule	Solvent	π-π* band (nm)	n-π* band (nm)	$\varepsilon_{325\,nm}$ (10⁴ L.mol⁻¹.cm⁻¹)
Azobenzene	MeOH	325	440	~2
Peptoid 1	MeOH	325	440	1.9
Peptoid 2	MeOH	325	440	4.4
Peptoid 3	MeOH	325	431	1.9
Peptoid 3	MeOH	325	434	4.4

- π-π* band and n-π* band unchanged

- Molar absorptivity > 2X for peptoids 3 and 4
  ➤ Interaction between chromophores

Photoisomerization experiments: LC-MS quantification of PSD

Peptoid solutions were irradiated with a Cosmedico Arimed B6 UV lamp (ca. 290-350 nm) to induce azobenzene isomerization. After different irradiation times, solutions were analyzed by liquid chromatography (Waters Alliance 2695) coupled to mass spectrometry (Waters QToF Premier, ESI (+)) in order to discriminate stereoisomers and to quantify the photostationnary distribution (PSD).

Peptoid 1
Z isomer 40 % *E isomer* 60 %

Peptoid 2
(Z,Z) 26 % *(Z,E) + (E,Z)* 33 % *(E,E)* 41 %

Peptoid 3
Z 48 % *E* 52 %

Peptoid 4
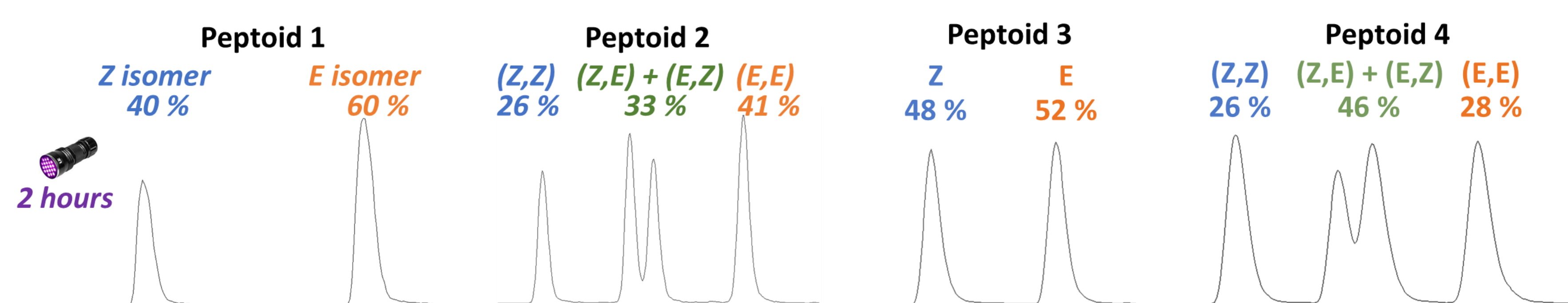*(Z,Z)* 26 % *(Z,E) + (E,Z)* 46 % *(E,E)* 28 %

2 hours

Figure 5. HPLC-MS analyzes of peptoids 1-4 after 2 hours of UV irradiation.

- Peptoids 1 and 2 : Z-isomer ~40 % in PSD

- Peptoids 3 and 4 : Z-isomer ~48 % in PSD

Z → E thermal retro-isomerization kinetics

Once the photostationnary state of a peptoid solution is reached, the solution remains in the LC autosampler where it stands at controled temperature and is protected from ambient light. This allows determinating the Z → E thermal retro-isomerization rate constant by measuring the overtime evolution of Z isomers.
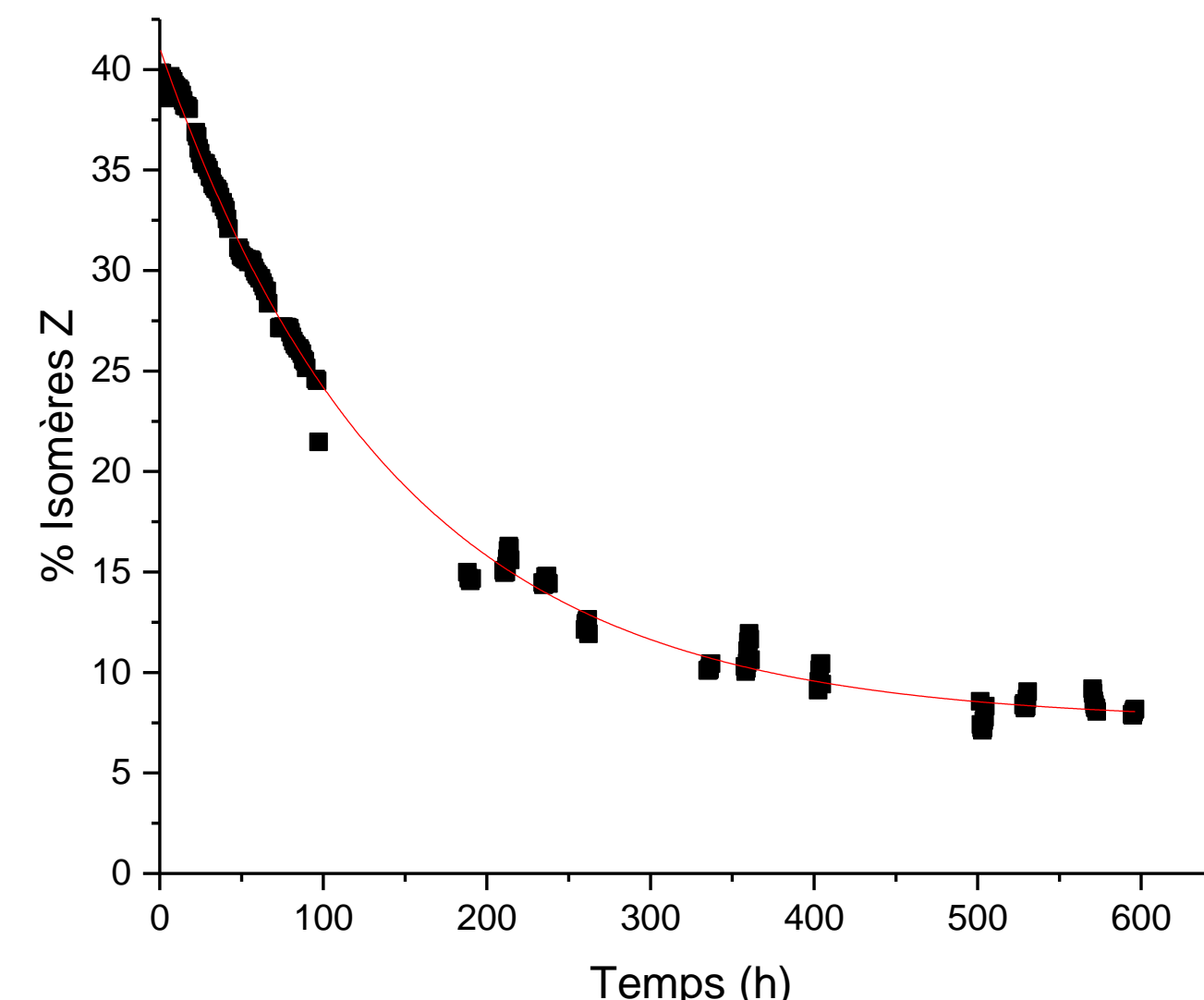

Figure 6. Peptoid 4 thermal retro-isomerization kinetics followed by LC-MS.

Molecule	Rate constant k (20°C) (10⁻⁶ s⁻¹)	$t_{1/2\ 20°C}$ (hours)
Peptoid 1	3.85	50
Peptoid 2	2.03	95
Peptoid 3	3.27	59
Peptoid 4	1.94	99

- $t_{1/2}$ peptoids 1 and 3 < $t_{1/2}$ peptoids 2 and 4
  ➤ Interaction between chromophores
- Ester Substitution barely increases $t_{1/2}$

Conclusions

With this work combining synthesis and photochemical characterization, we demonstrated that peptoids can be a good template to improve MOST properties of azobenzene. Indeed, by comparing peptoids containing one or two azobenzenes, we observed improvements of two key MOST parameters, *i.e.* molar absorptivity and half-life time. This suggests that interactions occur between the chromophores anchored on the peptoid backbone. Ester substitution of the azobenzene impact barely the MOST properties. Therefore, ester hydrolysis is the next step to complete.

References

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