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Supporting Information

Site Selectivity of Peptoids as Azobenzene Scaffold for Molecular Solar Thermal Energy Storage

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1. Peptoid synthesis

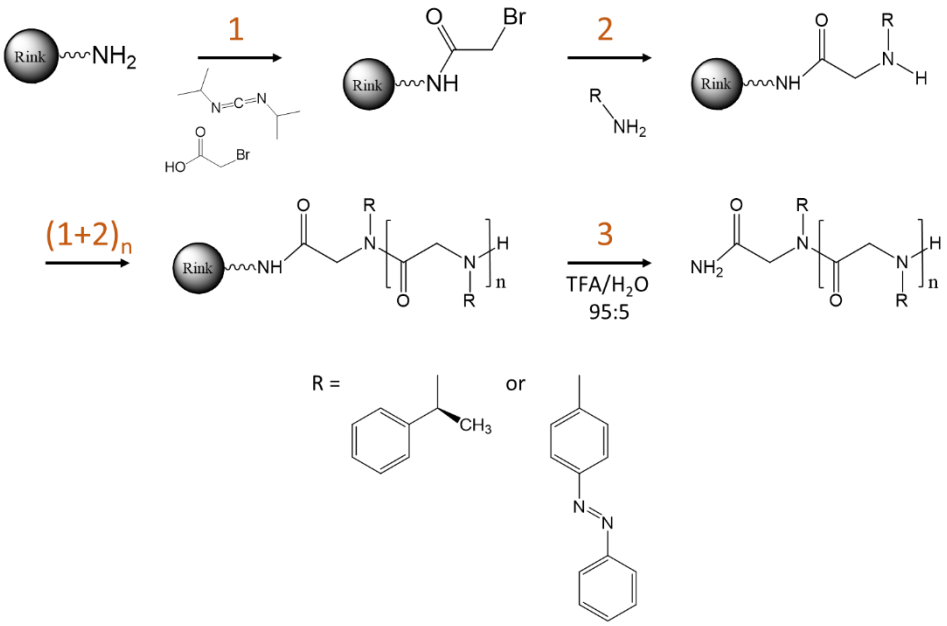

Figure S1. Peptoid solid-supported synthesis. Cycles of bromoacetylation assisted by N,N'-diisopropylcarbodiimide (1) and nucleophilic substitution by the primary amine of the desired side chain (2). Repetitions of steps 1 and 2 ($(1+2)_n$) give the peptoid with a defined size. Cleavage (3) from the resin using a trifluoroacetic acid/water solution allows to collect the peptoids as orange powders.

2. Peptoid characterization

Peptoid structures as well as their compositions, exact masses and molecular weights are shown on Figure S2.

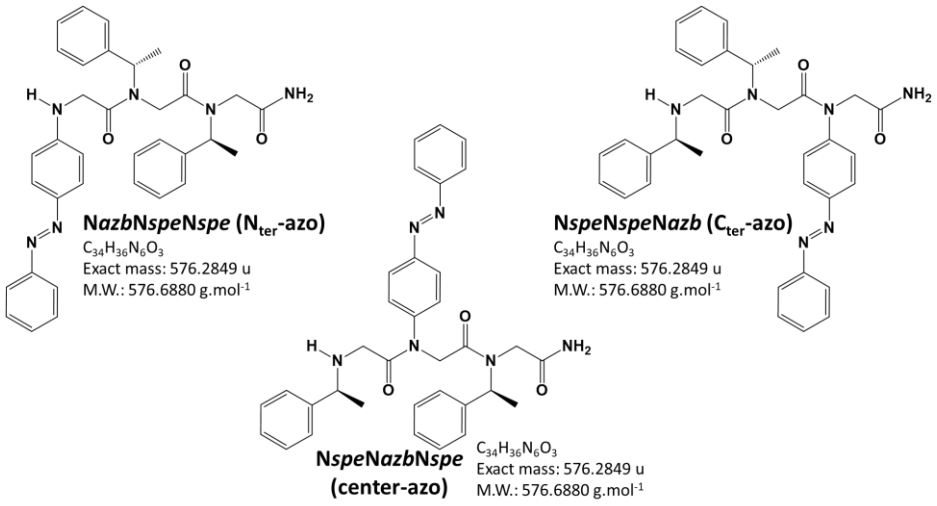

Figure S2. Structures, compositions, exact masses and molecular weights of the three peptoids studied.

Peptoids were characterized by mass spectrometry (MS) in positive ions mode on a QToF Premier (Waters, UK) equipped with an ElectroSpray ionization source. Typical analysis conditions were 1 mg.mL^{-1} peptoid solution in methanol (HPLC grade) diluted 1000× before injection in the mass spectrometer. Source settings for analysis are: Capillary 3.1 kV, Sampling Cone 30 V, Extraction Cone 5 V, Source Temperature 80 °C, Desolvation Temperature 120 °C, Nitrogen flow 500 L.h^{-1}.

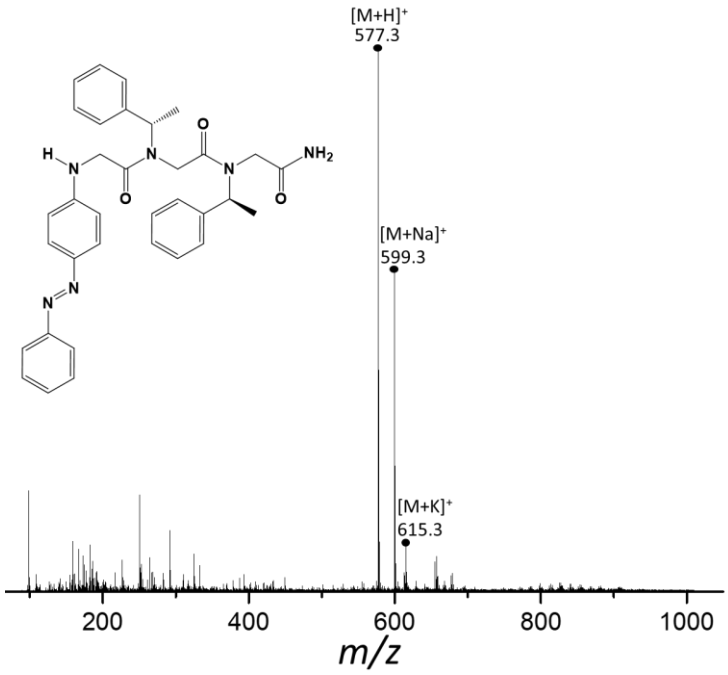

Figure S3. ESI mass spectrum for purified N_{ter}-azo. Signals at m/z 577 ($M+H^+$), m/z 599 ($M+Na^+$) and m/z 615 ($M+K^+$) confirm the presence of peptoid with 2 spe and 1 Azo units.

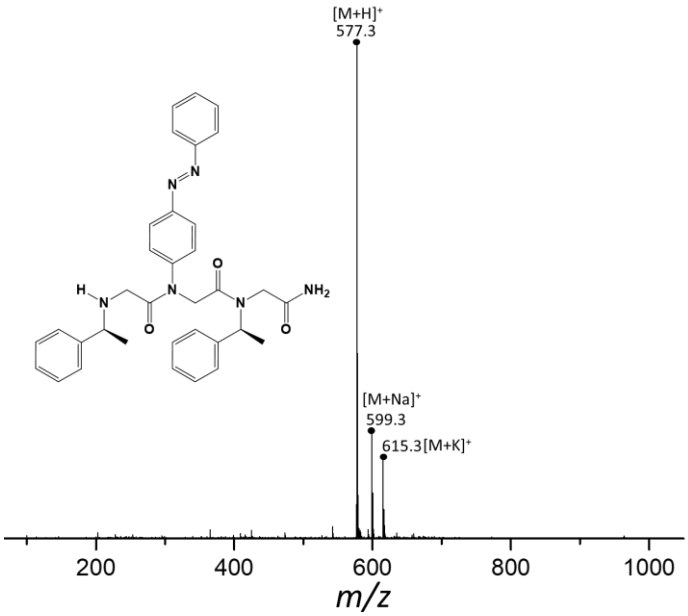

Figure S4. ESI mass spectrum for purified center-azo. Signals at m/z 577 ($M+H^+$), m/z 599 ($M+Na^+$) and m/z 615 ($M+K^+$) confirm the presence of peptoid with 2 spe and 1 Azo units.

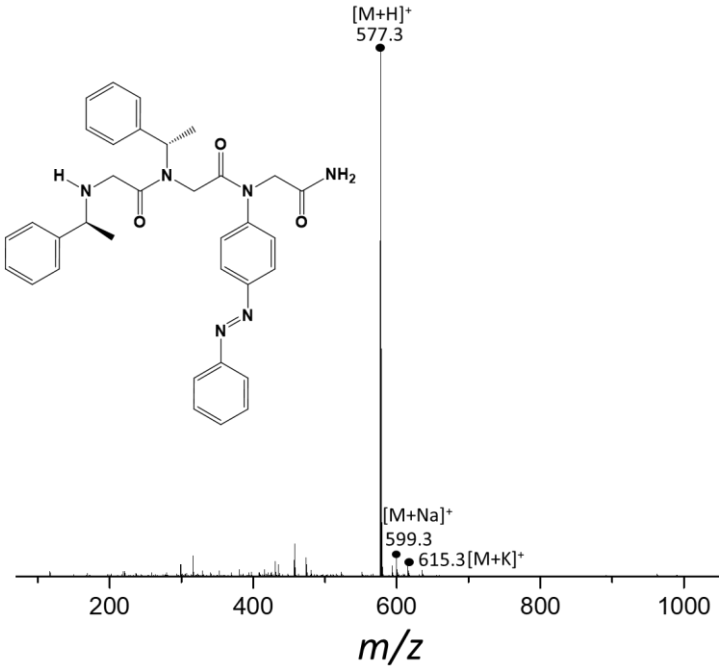

Figure S5. ESI mass spectrum for purified C_{ter}-azo. Signals at m/z 577 ($M+H^+$), m/z 599 ($M+Na^+$) and m/z 615 ($M+K^+$) confirm the presence of peptoid with 2 spe and 1 Azo units.

Figures S3 to S5 confirm the presence of peptoids with a molecular weight of 576 $g.mol^{-1}$ (2 spe and 1 Azo units) in the three samples. However, to have insights about their primary structures and to confirm the synthesis of the right sequences, tandem mass spectrometry experiments were performed (MS/MS). Collision-induced dissociation (CID) experiments were performed on protonated peptoids allowing to unravel the parent ions primary structure.
Similarly to peptides, peptoid fragmentation is mainly dominated by cleavages of their amide bonds, i.e. B/Y fragmentation. B ions possess the N terminus extremity intact after fragmentation while it is the C terminus extremity for Y ions. In addition to B/Y fragmentation, A/Y and Side Chain Loss (SCL) fragmentation patterns can also be observed for peptoids. More details and mechanistic insights are given in references [45] and [46].

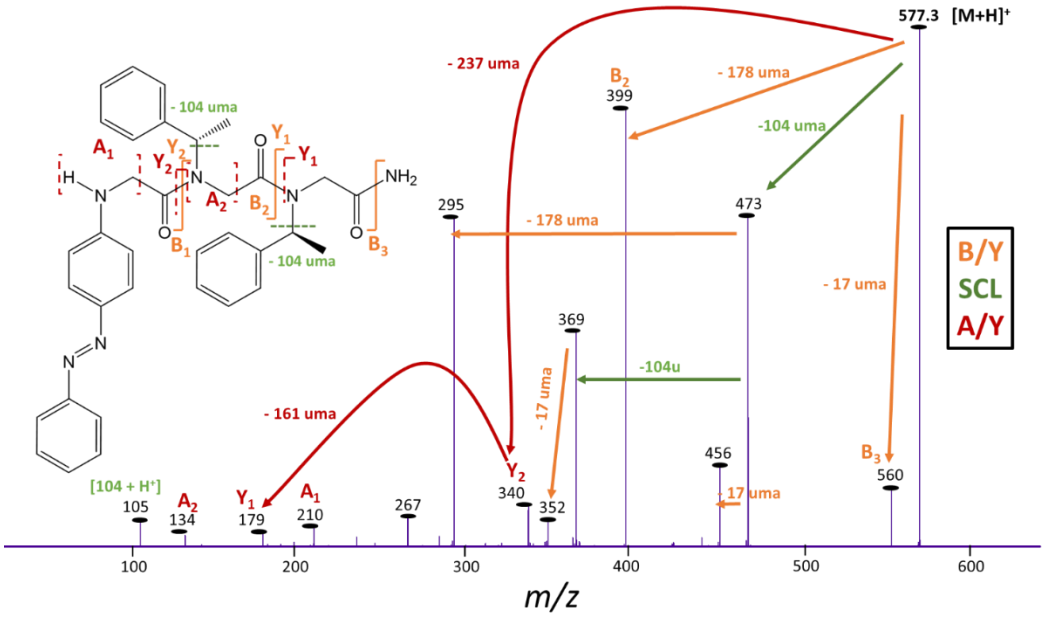

Figure S6. MS/MS spectrum of ions at m/z 577 ($M+H^+$) for N_{ter}-azo (Collision Energy: 15 eV).

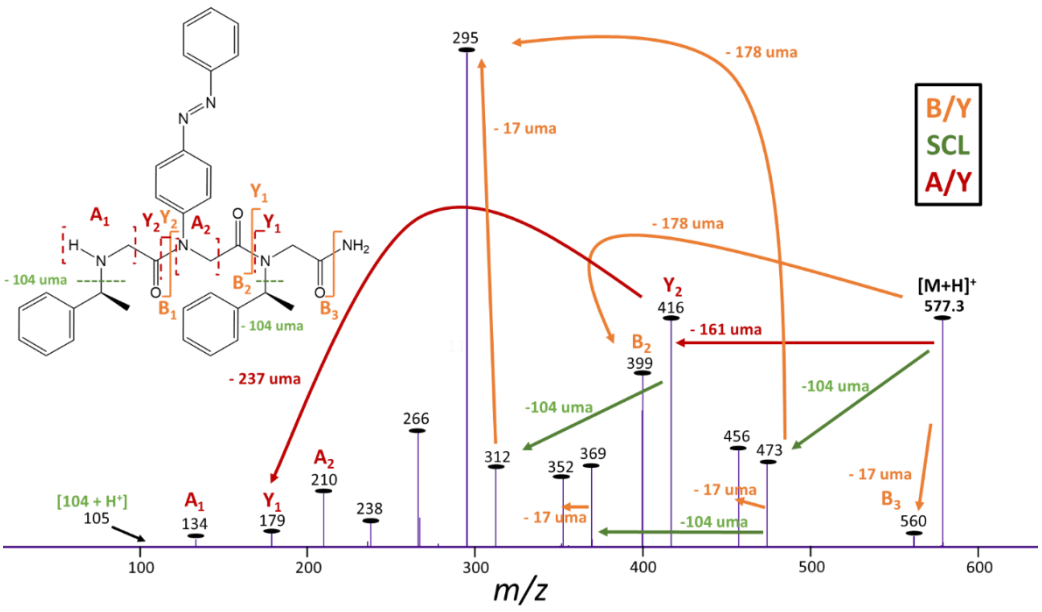

Figure S7. MS/MS spectrum of ions at m/z 577 ($M+H^+$) for center-azo (Collision Energy: 17 eV).

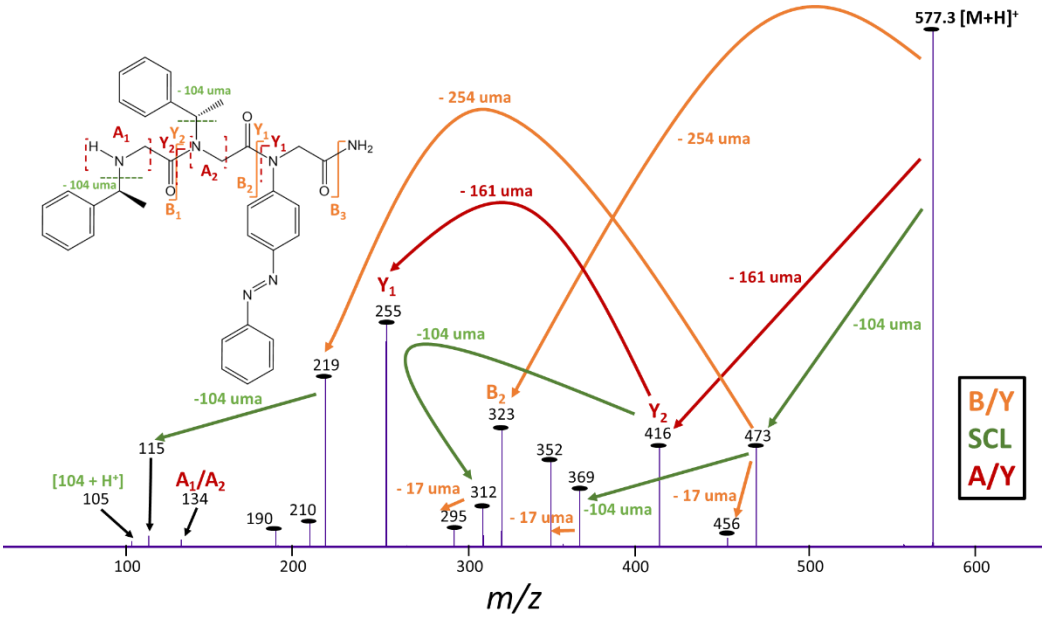

Figure S8. MS/MS spectrum of ions at m/z 577 ($M+H^+$) for C_{ter}-azo (Collision Energy: 15 eV).

Fragment identification based on peptoid structures combined to the three different MS/MS spectra confirm the expected sequence for each prepared isomer.

3. Irradiation source

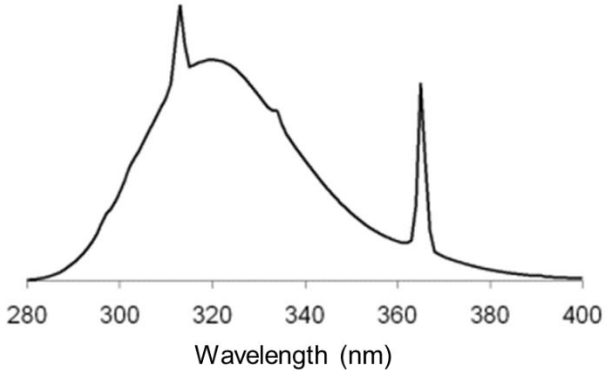

Figure S9. Emission spectrum of the Arimed B6 UV lamp (Cosmedico GmbH, Stuttgart, Germany). Power: 36 W ; Emission range approx. 290-350 nm ; Emission maximum approx. 300-320 nm. (Source: https://solariumzubehoer.eu/UVB-Therapielampe-Arimed-B6-36-W)

4. Molar extinction coefficients (ε)

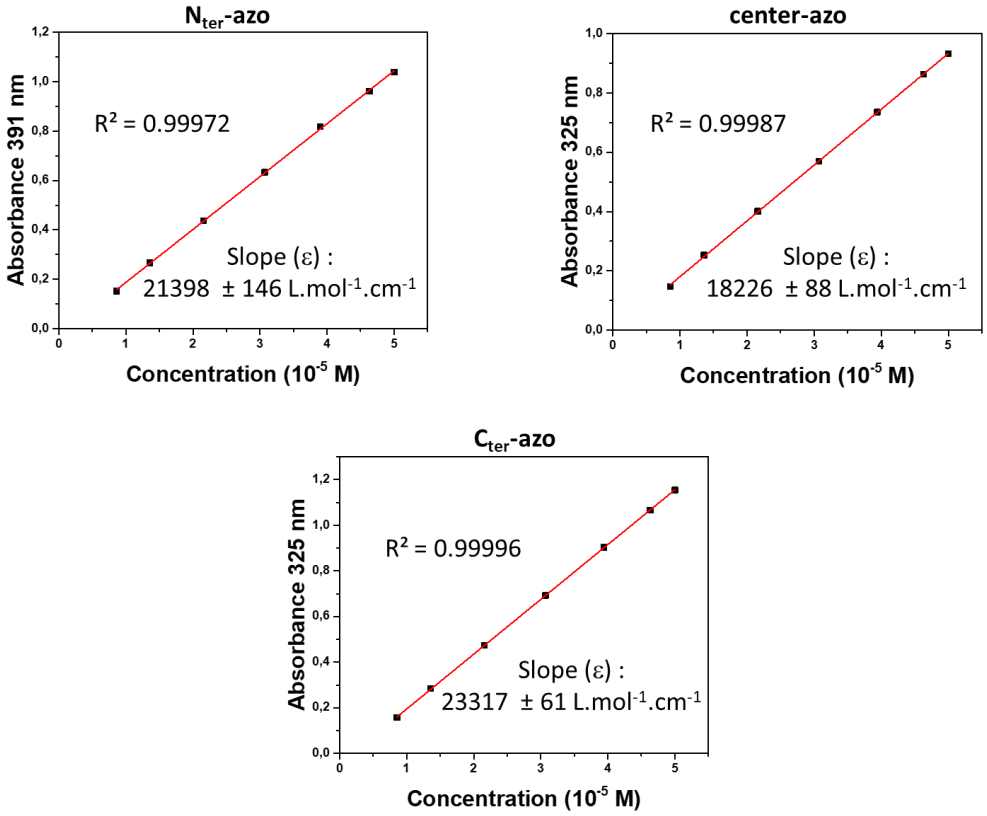

Figure S10. Measure of absorbance at λ_{max} for the three peptoids as a function of the concentration.

5. C_{ter}-azo photoisomerization

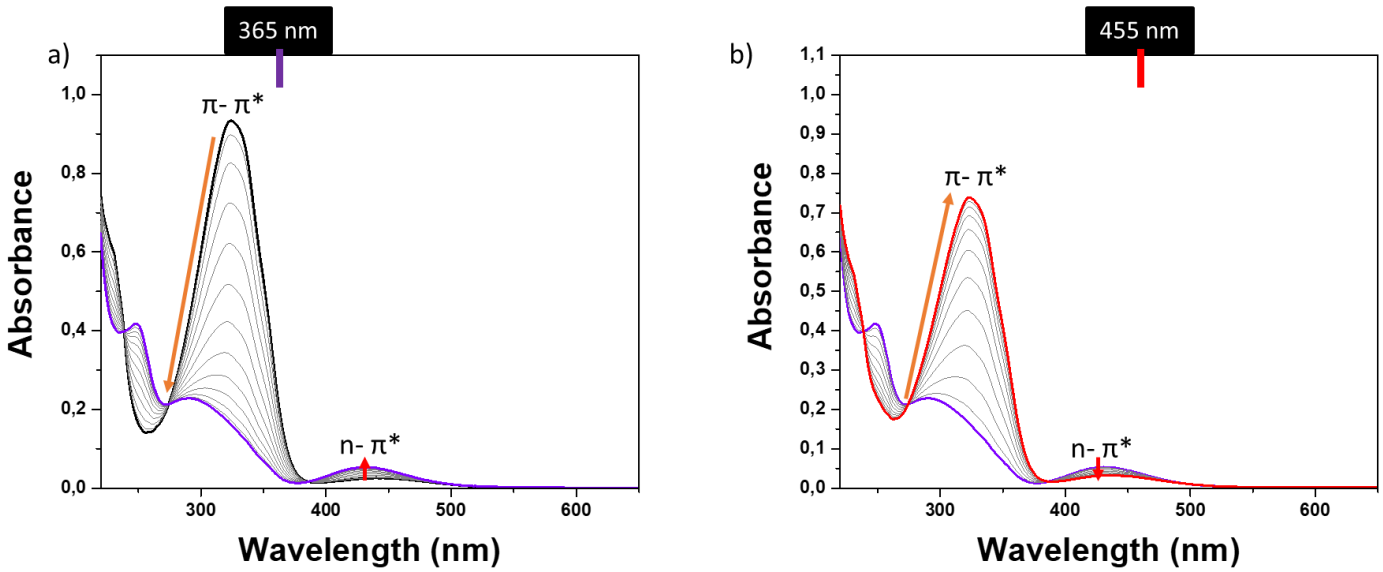

Figure S11. Isomerization monitoring of C_{ter}-azo by UV-Vis spectroscopy. a) 365 nm irradiation of C_{ter}-azo (MeOH, 3.9 10^{-5} M). The behaviour is typical of trans-cis azobenzene isomerization. b) 455 nm irradiation of C_{ter}-azo on the PSS generated by 365 nm irradiation. (MeOH, 3.9 10^{-5} M). The behaviour is typical of cis-trans azobenzene isomerization. Black line, no irradiation; purple line, UV-PSS; red line, vis-PSS.

Note that the concentration of the peptoid solution is lower than the one of center-azo (5.0 10^{-5} M) for this measurement (see **Figure 2 a** and **b** in the main text), this is why the absorbance is equivalent between the two peptoids despite their different molar extinction coefficient.

6. Photochemical stability

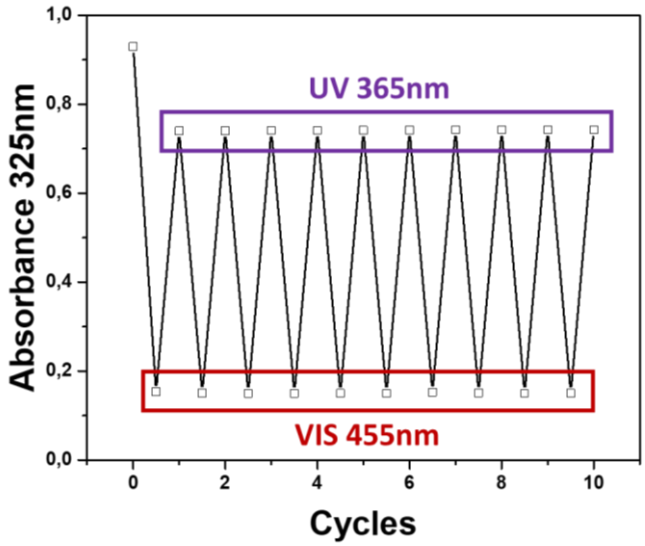

Figure S12. Absorbance measurement at λ_{max} (325 nm) after each 365 nm photoisomerization and 455 nm photochemical back-isomerization step for center-azo (MeOH, 5.10^{-5} M) during 10 cycles. No degradation was observed.

7. Thermal Z → E back-isomerization investigation by LC-MS

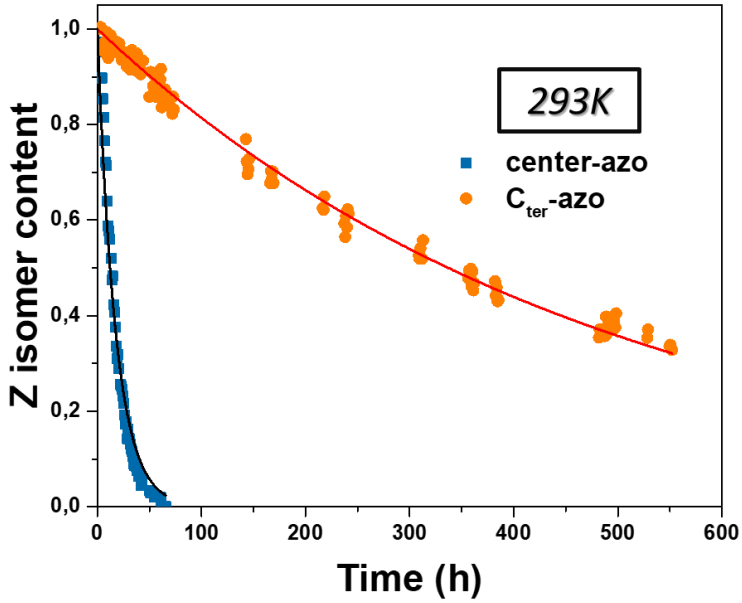

Figure S13. Normalized plots of Z isomer content as a function of the time spent in the dark (293 K) for center-azo and C_{ter}-azo peptoids monitored by LC-MS: center-azo (blue curve) presents a faster back-isomerization than C_{ter}-azo (orange curve). The black and red lines correspond to the first-order exponential fits.

Fitting data:

Table S1. Fitting data associated with the curves on Figure S13

	center-azo	**C_{ter}-azo**
Fitting equation	$y = y_0 + A\,e^{-kx}$ (with y_0 fixed to 0 and A fixed to 1)	
R^2	0.987	0.992
k (h^{-1})	0.05695	0.00206
k (s^{-1})	$1.58\ 10^{-5}$	$5.72\ 10^{-7}$

The extracted rate constants k were related to the half-life time by the following formula:

$$t_{1/2} = \frac{\ln(2)}{k}$$

References

[45] E. Halin, S. Hoyas, V. Lemaur, J. De Winter, S. Laurent, M. D. Connolly, R. N. Zuckermann, J. Cornil, P. Gerbaux, *J. Am. Soc. Mass Spectrom.* **2019**, *30*, 2726–2740.

[46] E. Halin, S. Hoyas, V. Lemaur, J. De Winter, S. Laurent, J. Cornil, J. Roithová, P. Gerbaux, *Int. J. Mass Spectrom.* **2019**, *435*, 217–226