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Title:

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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Abstract

Storing solar energy represents a major challenge in modern science. Chemical storage with **MO**lecular **Solar Thermal** systems (**MOST**) appears promising though challenging. 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. Among the MOST systems, azobenzene with its E → Z photoisomerization has been studied but characteristics such as storage enthalpy and half-life time must be improved. To do so, anchoring chromophores on a macromolecular backbone appears to be an elegant strategy since cooperative effects between chromophores may help enhancing these properties.

Our study consists of producing new MOST systems based on a peptoid-type backbone supporting azobenzene chromophores at key positions. This backbone could allow cooperative effects since peptoids are foldamers and can thus adopt specific

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secondary structures in solution. We synthesized different peptoids containing a single azobenzene chromophore at key positions using a solid-phase on-resin protocol. The peptoid sequences are confirmed based on MS and MS/MS analyses using the B/Y and A/Y fragmentation patterns typical of protonated peptoids. Under UV irradiation, different stereoisomers are produced, and their relative proportions are determined using LC-MS analyses. LC-MS also allows the determination of the photoisomers half-live times ($t_{1/2}$) by performing continuous analyses while the solutions are kept in the dark at controlled temperatures. Interestingly, the backbone position of the azobenzene chromophore strongly modifies its photoisomerization and retro isomerization properties. We for instance measured $t_{1/2}$ ranging from 0.5 to 11 days in solution (20 °C) compared to 4 days for pristine azobenzene. We are currently measuring $t_{1/2}$ at different temperatures to have access to the kinetics parameters of the thermal retro-isomerization, i.e. activation energy.

Another interesting aspect of this study is the use of tandem ion mobility (IMS-IMS) experiments on an original instrument (at ULyon) based on two drift tubes that are separated by an ion trap that could be fixed at a determined temperature. This allows monitoring the gas-phase retro-isomerization kinetics of protonated peptoids at different temperatures. This gives access to rate constants and activation energies for our original MOST systems in the gas phase (**Figure 2**). These values are compared to the solution data to highlight the influence of the ionization and/or solvent evaporation on the kinetics of the isomerization processes.

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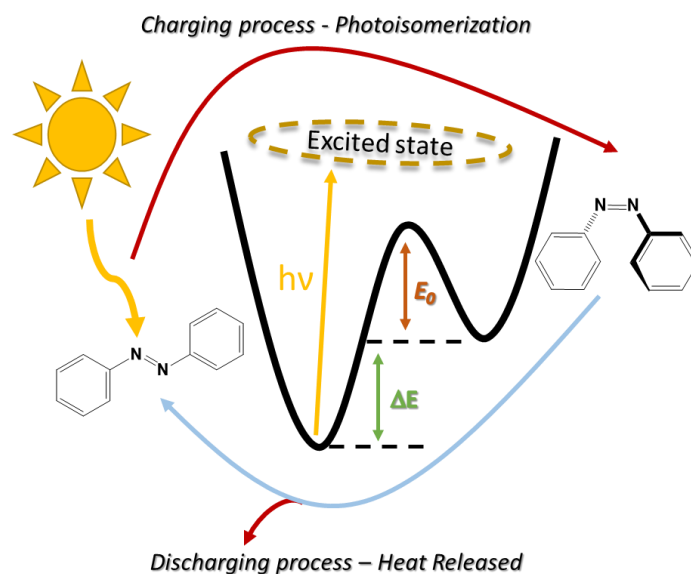


Figure 1. Working principle of azobenzene as a MOST system: E-azobenzene is irradiated by solar light and is photo-isomerized to the Z-isomer. This isomer stores the energy, ΔE , for a certain time. Energy is then released as heat during the thermal back-reversion to yield back E-azobenzene.

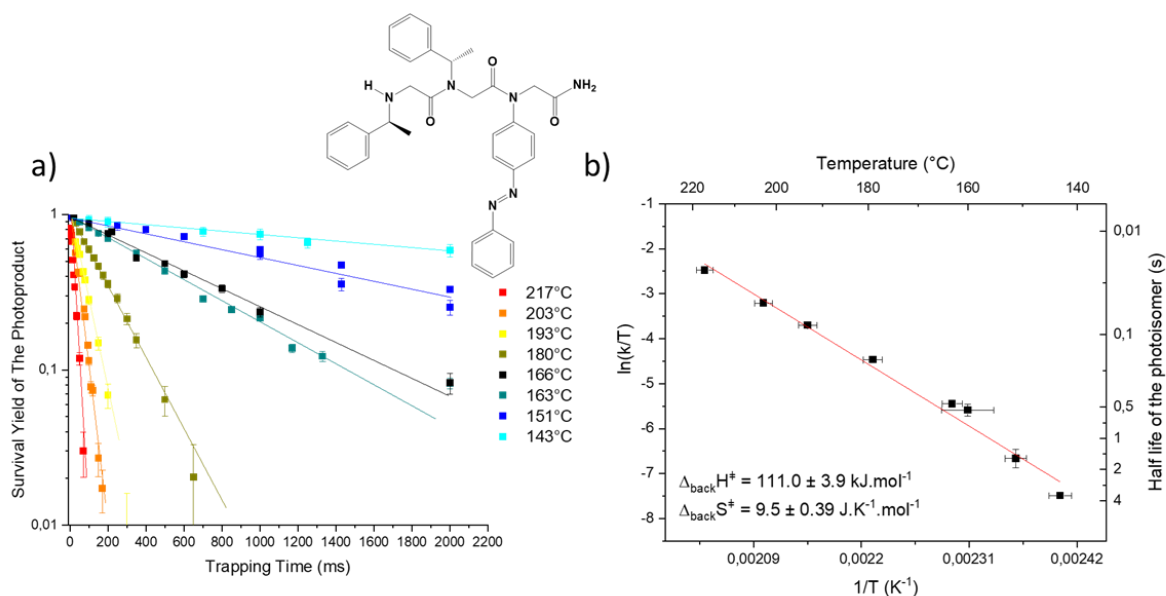


Figure 2. a) Kinetics study at different temperatures using tandem IMS. b) Eyring's plot giving access to the kinetics parameters.

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