

Untangling the operation mechanism of a light-driven phenylazoimidazolium out-of-equilibrium molecular machine

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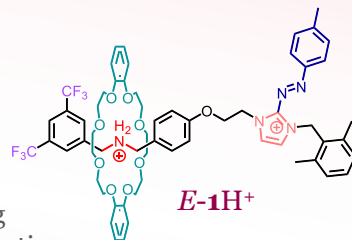
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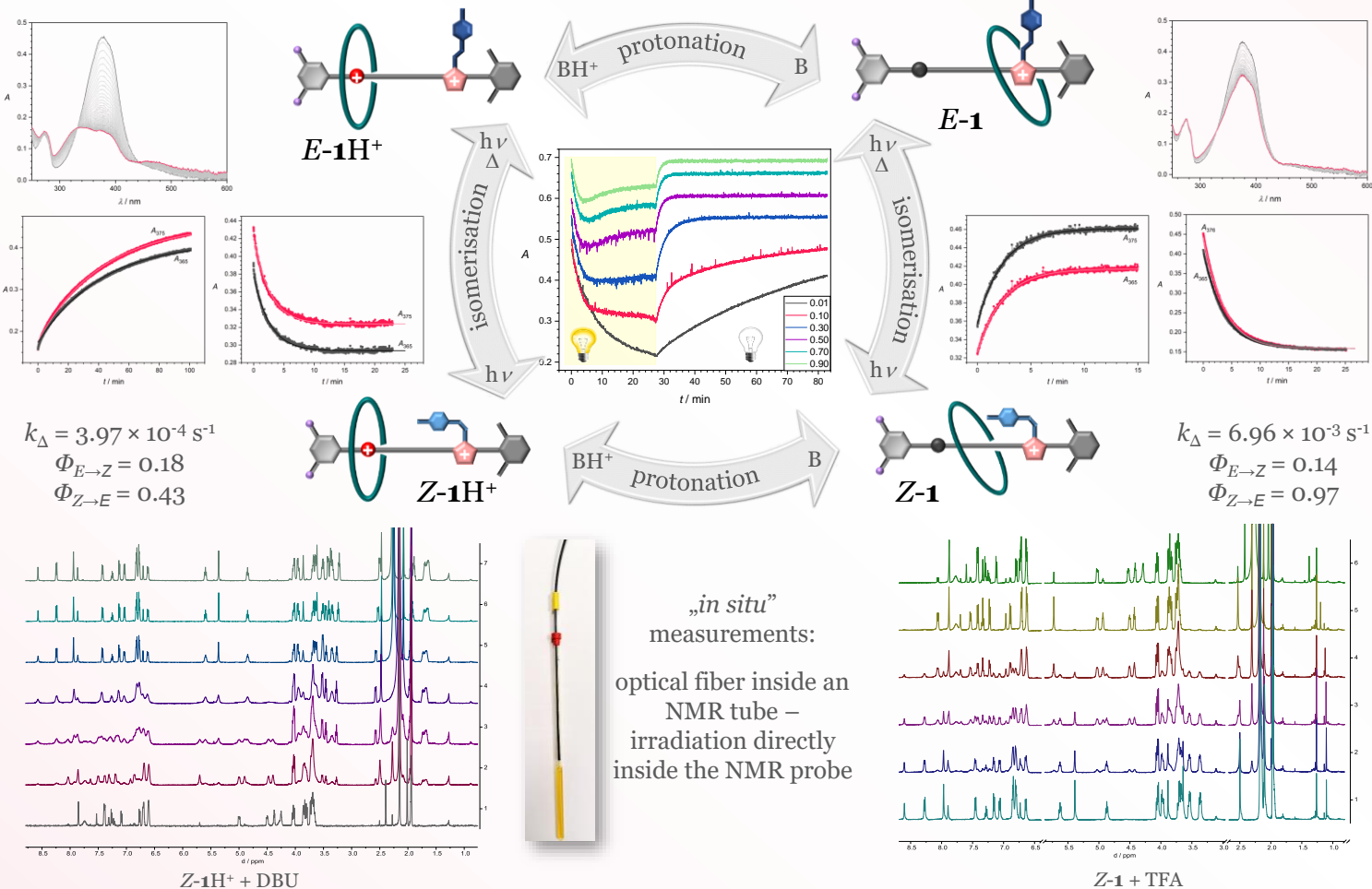
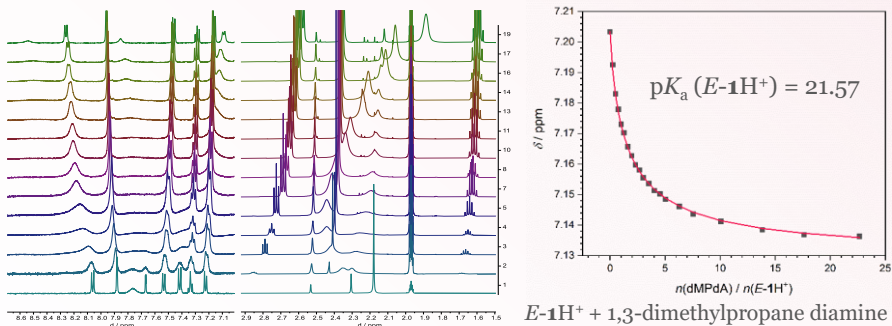
INTRODUCTION

Rotaxanes, whose properties are directed by supramolecular interactions between its components, often serve as a platform for design of molecular machines: systems that perform mechanical movements as a result of an appropriate external stimulus.¹

We present a rotaxane-based system that can be operated by application of two external stimuli: light (inducing isomerisation of the photoswitchable phenylazoimidazolium) and pH (inducing deprotonation of the ammonium site), leading to the formation of four interconverting species which differ amongst each other by thermodynamic, photophysical, and chemical properties.



- the operation mechanism of this molecular machine was studied in acetonitrile using spectrophotometry and NMR spectroscopy
- four-stage operation cycle:
two protonation/deprotonation +
two isomerisation/backisomerisation
equilibria
- individual and combined steps were studied in the conditions of constant „in situ” irradiation and in the dark



CONCLUSIONS

- the system behaves as an autonomous molecular machine when operated in the conditions of constant irradiation
- cycling occurs in counter-clockwise direction
- Z-form of the protonated species is more acidic than its E-form
- backisomerisation of the Z-species is fast, even more so for the deprotonated form

LITERATURE

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