AZOBENZENE PHOTOSWITCHES : OBSERVING MOLECULES SWITCHING USING ION MOBILITY MASS SPECTROMETRY

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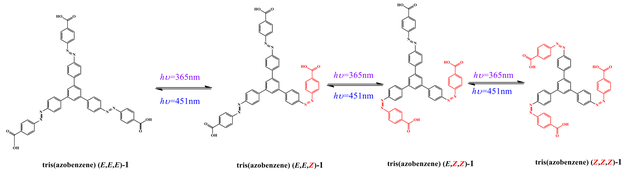
Overview

- ***Purpose*:** Multi-photochromic C_3-symmetric switching molecules have been investigated by Ion Mobility Mass Spectrometry (IMMS)
- ***Methods:*** ESI-IMMS and ESI-MS-IMMS experiments were carried out before and after UV-irradiation
- ***Results:*** All azobenzene isomers were efficiently separated by IMMS and collisional activation back-switching experiments were also conducted

Introduction

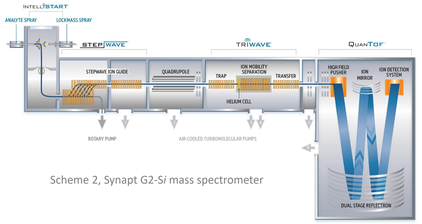
Molecules and supramolecules that are capable to undergo structural rearrangements when subjected to an external stimulus have attracted a great deal of attention as they can represent the key building blocks for the fabrication of responsive molecular devices.[1] Sophisticated dynamic functions are at the basis of many processes in Nature, ultimately ruling the most complex phenomena of life. Such a plethora of complex functions takes place in chemical systems which are able to respond to a variety of independent inputs including chemical, electrochemical and photochemical stimuli.[2] The use of photons has been regarded as one of the most promising for technological application thanks to the possibility of remote application with high spatiotemporal resolution, without generating waste products. Recently, increasing interest has been devoted to the design and synthesis of multi-photochromic architectures. Here is reported a novel class of star-shaped multi-azobenzene photoswitches comprising individual photochromes connected to a central trisubstituted 1,3,5-benzene core (Scheme 1). The unique design of such C_3-symmetric molecules, consisting of conformationally rigid and pseudo-planar scaffolds, made it possible to explore the role of electronic decoupling in the isomerization of the individual azobenzene units. The electronic decoupling provided by this molecular design guarantees a remarkably efficient photoswitching of all azobenzenes, as evidenced by their photoisomerization quantum yields, as well as by the Z-rich UV photostationary states. Ion mobility mass spectrometry (IMMS) was efficiently exploited to study multi-photochromic compounds revealing the occurrence of a large molecular shape change in such rigid star-shaped azobenzene derivatives.



Scheme 1, tris(azobenzene) (**1**) considered in the current study and its three isomers

Methods

Ion Mobility Spectrometry: The experiments were performed by using a hybrid quadrupole (Q)–traveling wave ion mobility (TWIMS)–time-of-flight (ToF) mass spectrometer (Synapt G2-*Si*, Waters, U.K.) equipped with an ESI source (negative mode) *(Scheme 2)*. We injected the sample solutions in the instrument by either direct infusion, or by using a HPLC setup (mentioned previously) to separate the isomers of **1** prior to analysis. Typical ion-source conditions were capillary voltage 2.5 kV, sampling cone 30 V, source offset 80 V, source temperature 100 °C, and desolvation temperature 200 °C. The parameters of the Stepwave were tuned to avoid in-flight isomerization in the ion transfer regions of the mass spectrometer. The Stepwave 2 wave height was reduced to 0 and the Stepwave RF-Offset was lowered to 50. The collisional activation experiments were performed on single isomers of **1** by previously isolating them by HPLC. Mass-selected ions were subjected to collisions with increased voltages in the Trap cell and subsequently separated and analyzed by IMMS. We worked at low Trap CE in order to avoid collision-induced decomposition of the ions. CCS were determined by using negative polyalanine and an in-house developed procedure.[3,4]



Scheme 2, Synapt G2-*Si* mass spectrometer

Results & Discussion

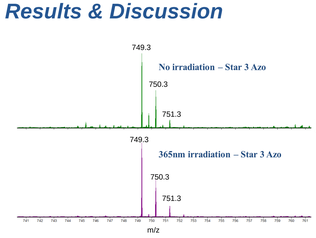


Figure 1, ESI mass spectra recorded for **1** before and after light irradiation

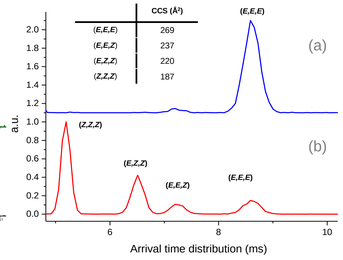


Figure 2,Arrival Time Distributions (ATD) recorded for **1** before (**a**) and after (**b**) UV-light irradiation

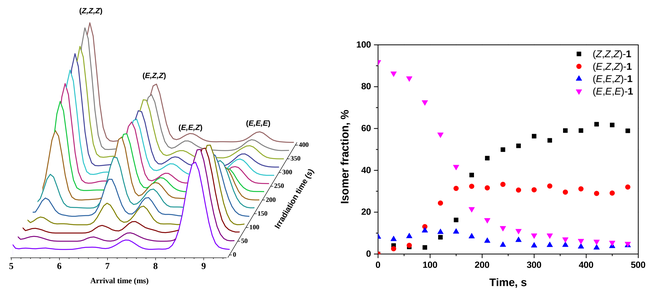
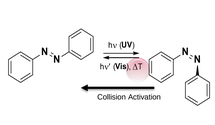
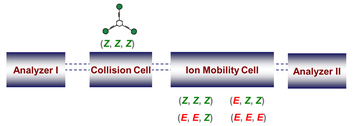


Figure 3, Photoisomerisation of **1** followed by IMMS. Syringe containing a solution of **1** was irradiated with UV-light (365nm) during direct infusion followed by IMMS separation. Left, temporal evolution of the arrival time distributions. Right, isomer fraction over time determined by integration of the IMMS signals.



Scheme 2, thermal back-isomerization



Scheme 3, Setup for inducing and probing the thermal isomerization by collisional heating

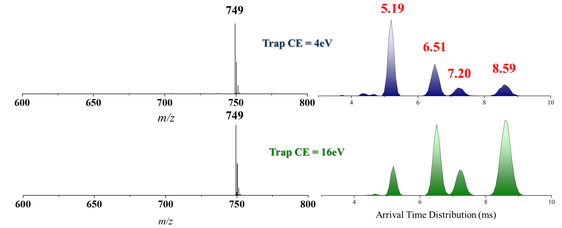


Figure 4, Z → E isomerization of azobenzene ions by collisional activation, prior to their separation by ion mobility mass spectrometry. It is worth to note that step wave conditions are critical because can induce isomerization before IMMS investigation.

Finally, we investigated the possibility to induce the in-flight *Z* → *E* isomerisation of azobenzene ions by collisional activation, prior to their separation by ion mobility. In this case, we employed an HPLC set-up to separate the four isomers before injection in the mass spectrometer and performed the aforementioned experiments on the isolated photogenerated (*Z,Z,Z*)-**1** isomer. After HPLC separation, the isomers of **1** are mass-selected with the quadrupole mass selector and are then subjected to collisional heating (collisional activation) prior to the ion mobility separation by gradually increasing their kinetic energy within the Trap cell (Scheme 2).

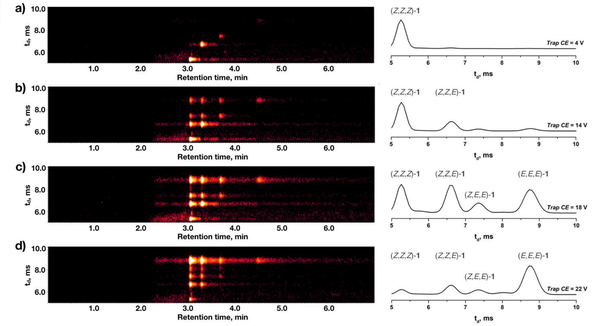


Figure 5, Collisionally-induced Z → E isomerisation of the (*Z,Z,Z*)-**1** ions at different collision energies (Trap CE). a) Trap CE = 4 V; b) Trap CE = 14 V; c) Trap CE = 18 V; d) Trap CE = 22 V. Left, 2D IMMS/HPLC-MS data recorded for [1-H⁺]⁻ at m/z 749.2 : HPLC retention time reported on x axis, ion mobility drift time on y axis. . Signal at 3 min 5 s retention time corresponds to (*Z,Z,Z*)-**1**, 3 min 20 s (*Z,Z,E*)-**1**, 3 min 40 s (*Z,E,E*)-**1**, 4 min 30 s (*E,E,E*)-**1**. Right, Arrival time distributions recorded at various Trap CE for the HPLC signal appearing at 3 min 5s and corresponding to (*Z,Z,Z*)-**1**.

Conclusions

In summary, IMMS has been proved to be an efficient technique to investigate the photo-isomerization of switching molecules such C_3-symmetrical tris(azobenzene). Moreover, the quantitation of each isomers versus irradiation time was achieved. Finally, the in-flight Z → E isomerisation has been investigated by combining HPLC and IM separation. A more complete study can be found at the following reference : J. Am. Chem. Soc., DOI: 10.1021/jacs.9b02544 (“***A new class of rigid multi(azobenzene) switches featuring electronic decoupling: unravelling the isomerization in individual photochromes”***).

References

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Acknowledgments

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