AZOBENZENE PHOTOSWITCHES : OBSERVING MOLECULES SWITCHING USING ION MOBILITY MASS SPECTROMETRY

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Overview

• Purpose: Multi-photonionic C₂-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 illumination.

Results

All azobenzenes 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. 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 capable to respond to a variety of independent inputs including chemical, electrochemical and photochemical stimuli. 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-photonic architectures. Here is reported a novel class of star-shaped multi-azobenzene photochromes comprising individual photochromes connected to a central tri-substituted 1,3,5-benzen core (Scheme 1). The unique design of such C₂-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 azobenzenes units. The electronic decoupling provided by this molecular design guarantees a remarkably efficient photoisomerization of all azobenzenes, evidenced by their photostabilization quantum yields, as well as by the Z-rich UV photostabilized states. Ion mobility mass spectrometry (IMMS) was efficiently exploited to study multi-photonic compounds revealing the occurrence of a large molecular shape change in such rigid star-shaped azobenzene derivatives.

Methods

Ion Mobility Spectrometry: The experiments were performed by using a hybrid quadrupole (Q)-travelling wave ion mobility (TWIMS)–time-of-flight (ToF) mass spectrometer (Synapt G2-S, Waters, UK) 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 pump (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 declustering temperature 200 °C. The parameters of the Stepwave were tuned to avoid in-flight isomerization in the ion transfer regime of the mass spectrometer. The Stepwave 2 wave height was reduced to 150 V and the Stepwave RF-Off was lowered to 50 V. 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 and analyzed by IMMS. We worked at low Trap CE in order to avoid collision-induced decomposition of the ions. CCS were determined by negative pentafluoropropionyl and an in-house developed procedure.¹,²

Results & Discussion

Finally, we investigated the possibility to induce in the right 2 – Z isomerization 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) ions. After HPLC separation, the isomers of 1 are mass-separated 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).

Conclusions

In summary, IMMS has been proved to be an efficient tool to investigate the photoswitching of molecules such as C₂-symmetric triisocyanobenzene. However, the quantification of each isomer versus irradiation time was achieved.

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References
¹ For the definition of different types of photochromism, see: Balzani, V., et al. Prog. Photochem. 1970, 10, 1-44.
² For the details of methodology used for this experiment, see: Baker, T. M., et al. Analyst 2017, 142, 2571, 9593-9599.
³ Wenz, G.; Angerer, C.; Brav pp2 2017, 18, 1271, 11090-11075.