Self-Assembled Monolayers of Azobenzene Derivatives : on the use of Mass Spectrometry to Monitor Photo and Back Isomerization Reactions

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Introduction

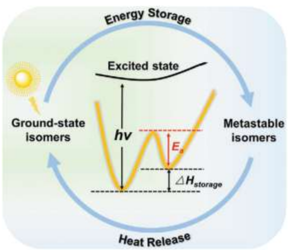


Figure 2: The solar thermal conversion of molecular photoswitches and their storage mechanism [1].

Photoswitches constitute one of the most ubiquitous and versatile classes of stimuli-responsive molecular systems. A fundamental prerequisite for integrating photoswitchable moieties into adaptive materials is a detailed understanding of their switching behavior. Among these, azobenzenes (AZO) undergo reversible photoisomerization between the ground-state trans (E) configuration and the metastable cis (Z) configuration (**Figure 1**). When energy is needed, the metastable isomers can be converted back to the stable isomers by spontaneous thermal decay processes or upon catalysis, releasing the excess energy in the form of heat while recovering the parent isomers (**Figure 2**) [1]. Despite being among the most extensively studied photoswitches, azobenzenes still suffer from limitations related to incomplete photoisomerization yields and weak thermal half-life of the Z-isomers upon red-shifting the absorbance to match solar irradiation or for biomedical applications [1,2].

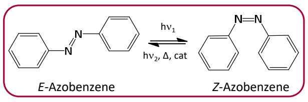


Figure 1: The isomerization reaction of azobenzene.

Strategy

Densely packed self-assembled monolayers (SAM) of azobenzene derivatives anchored on rigid substrates exhibit a high yield of photoisomerization due to cooperative switching effects [3]. The goal of our study is to prepare azobenzene chromophores end-terminated by alkyne groups to perform a click reaction with an azide which will be grafted onto different substrates. Glass and ITO (Indium-Tin-Oxide) are ideal substrates for this work thanks to their transparency and chemisorption efficiency with either silane or phosphonic acid groups respectively [4]. The determination of the properties of the isolated chromophores was performed before the SAM preparation to assess the impact of alkyne group and substituents on the chromophore photoswitching properties and to further evaluate the role of intermolecular interactions within the close-packed assemblies on the photoswitch properties.

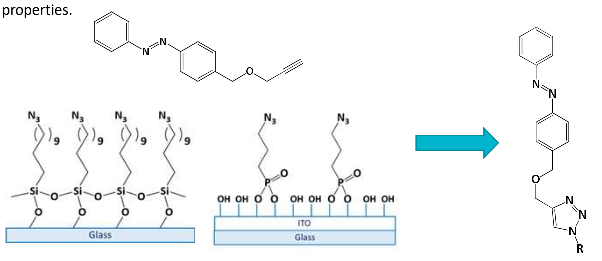
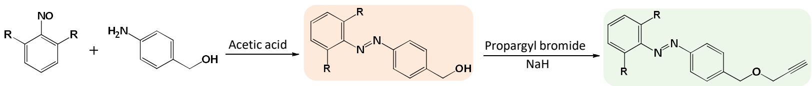


Figure 3: Azobenzene grafting on glass or ITO.

Synthetic procedure



RMN vs LC-MS to learn about ionization efficiency

A vial containing a solution of 5 mg of AZO in 600 µl of deuterated acetonitrile was irradiated with a lightningcure LC8 L9588-02A UV lamp (ca. 220 - 400 nm) to induce isomerization. Two types of analyses were performed in parallel on the same sample, and a total of three replicates were conducted for each of the two molecules. First, 1 µl is withdrawn from the vial after irradiation and diluted in 1.5 ml of HPLC-grade acetonitrile to perform an analysis by liquid chromatography (Waters Alliance 2695) coupled to mass spectrometry (Waters QToF Premier, ESI (+)), This allows the two isomers to be separated and quantified by integrating the area under the two peaks of the Extracted Ion Current (EIC) chromatograms of the $[M+H]^+$ ions, At the same time, an NMR analysis (using a Bruker AVANCE II 500 spectrometer (500 MHz)) is performed on the remaining solution in the irradiated vial. By integrating the two peaks corresponding to the two isomers (Z and E) of the two types of aliphatic protons, it is also possible to determine the percentage of each isomer.

AZOH alkyne

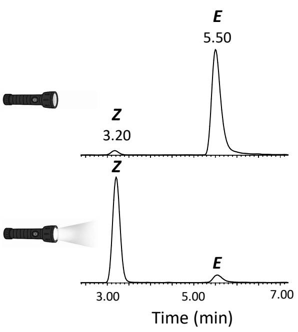


Figure 4: LC-MS analysis (EIC chromatogram of the $[M+H]^+$ ions at m/z 251) for AZOH alkyne.

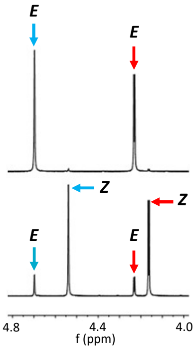
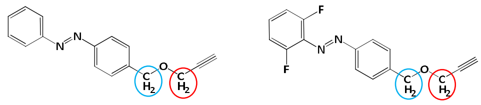


Figure 5: RMN analysis of AZOH alkyne.



	% cis	% trans
RMN	82.3 ± 0.8	17.7 ± 0.8
LC	81.1 ± 0.1	18.9 ± 0.1

	% cis	% trans
RMN	70.3 ± 0.2	29.7 ± 0.2
LC	69.4 ± 0.3	30.1 ± 0.3

$AZOF_2$ alkyne

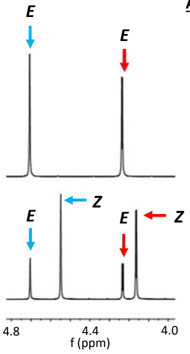


Figure 6: RMN analysis of $AZOF_2$ alkyne.

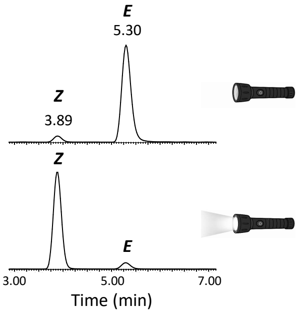


Figure 7: LC-MS analysis (EIC chromatogram of the $[M+H]^+$ ions at m/z 287) for $AZOF_2$ alkyne.

Thermal back isomerization : LC-MS analyses

The AZOH alkyne and the $AZOF_2$ alkyne in acetonitrile (10^{-6} g/ml) were irradiated with a lightningcure LC8 L9588-02A UV lamp (ca. 220 - 400 nm) for 2 minutes to induce isomerization. The solutions were stored in a stove at 60°C, in the dark. LC-MS analyses were performed to investigate the thermal back isomerization by measuring the decrease of the Z isomer contribution over the time. By plotting the Z isomer contribution as a function of time, an exponential was obtained whose slope corresponds to the rate constant (k) used to calculate the half-life time ($t_{1/2}$). Two replicates were done for each azobenzene and the average is in the table.

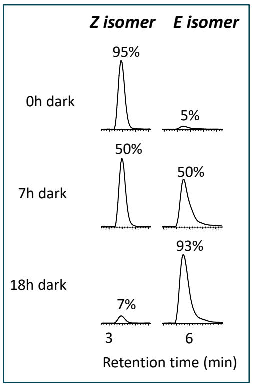


Figure 8: LC-MS analysis (EIC chromatogram of the $[M+H]^+$ ions at m/z 251) for AZOH alkyne.

60°C	k (10^{-6} h^{-1})	t ½ (h)
AZOH alkyne	29.66 ± 0.11	6.50 ± 0.03
$AZOF_2$ alkyne	3.42 ± 0.06	56.29 ± 1.07

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

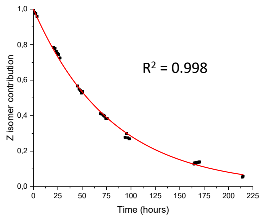


Figure 9: Plot of the Z isomer contribution for $AZOF_2$ alkyne as a function of time.

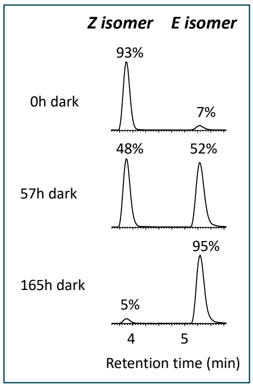


Figure 10: LC-MS analysis (EIC chromatogram of the $[M+H]^+$ ions at m/z 287) for $AZOF_2$ alkyne.

Kinetics parameters : Eyring plot

Using LC-MS kinetic studies, it is possible to determine the kinetic parameters (activation enthalpy and entropy) of these two photoswitches. To do this, kinetic studies were conducted at different temperatures. This allows us to determine the kinetic constant at a given temperature. For each of the two molecules, LC-MS analyses were performed at four different temperatures, with three replicates for each. By plotting 1/T against ln(k/T), we obtain a linear regression where the slope is $-\Delta H^\ddagger/R$ and the y-intercept is $-\Delta S^\ddagger/R$.

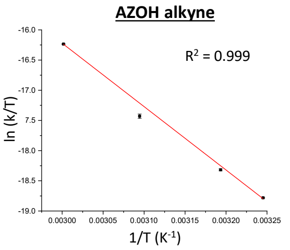


Figure 11: Plot of ln (k/T) for AZOH alkyne as a function of temperature.

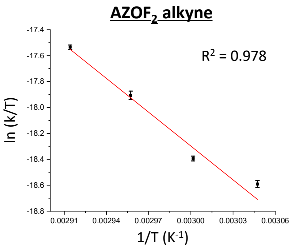


Figure 12: Plot of ln (k/T) for $AZOF_2$ alkyne as a function of temperature.

Slope = $-\Delta H^\ddagger/R$ $x_0 = -\Delta S^\ddagger/R$

	$\Delta H^\ddagger$ (kJ/mol)	**$\Delta S^\ddagger$ (J /mol K)**
AZO pristine	94,9	-44
AZOH alkyne	87.3 ± 1.5	-70.5 ± 4.5
$AZOF_2$ alkyne	72.3 ± 7.7	-132.9 ± 22.9

Conclusions

In this work, we prepared azobenzene derivatives bearing an alkyne group in order to click the azobenzenes onto ITO or glass via phosphonic acid groups or silanes respectively. We carried out analyses on two azobenzenes. By comparing the two analytical techniques—NMR and LC-MS—it was determined that the ionization efficiency of the two isomers is identical. Consequently, kinetic studies were conducted at different temperatures to determine their kinetic parameters using the Eyring equation. This demonstrates that the addition of fluorine atoms influence the properties as mentioned in the literature [5]. The next steps will be to graft the azobenzene derivatives onto ITO or glass to obtain SAMs and to carry out analyses to evaluate the properties of these systems.

Acknowledgments

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References

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