

Self-Assembled Monolayers Based on Azobenzene Derivatives as MOST Systems

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Introduction

Specially designed molecules that undergo light-induced isomerization to a metastable energy-rich isomer can be used to store solar energy. Such systems are known as MOlecular Solar Thermal systems (MOST). Exposing the compound to sunlight generates a high energy photoisomer that can then be stored for later use depending on its half-life time. 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 1) [1]. Azobenzene (AZO) derivatives are part of the MOST and exhibit a reversible photoisomerization between groundstate trans (E) and metastable cis (Z) form (Figure 2). However, some of their properties need to be improved for MOST applications such as the half-life time, the storage energy and the overlap between the solar spectrum and the absorption profile of the stable isomer [1,2].

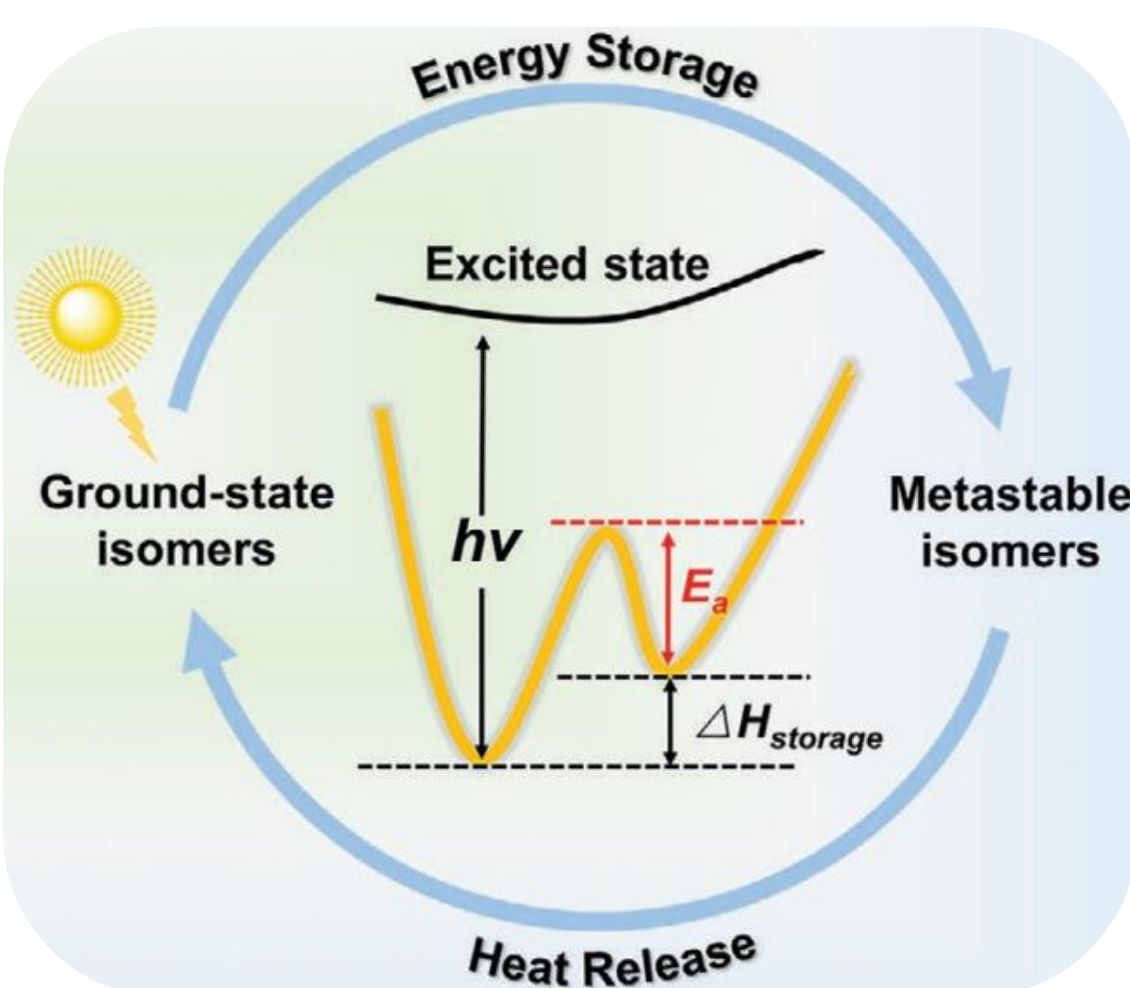


Figure 1: The solar thermal conversion of molecular photoswitches and their storage mechanism [1].

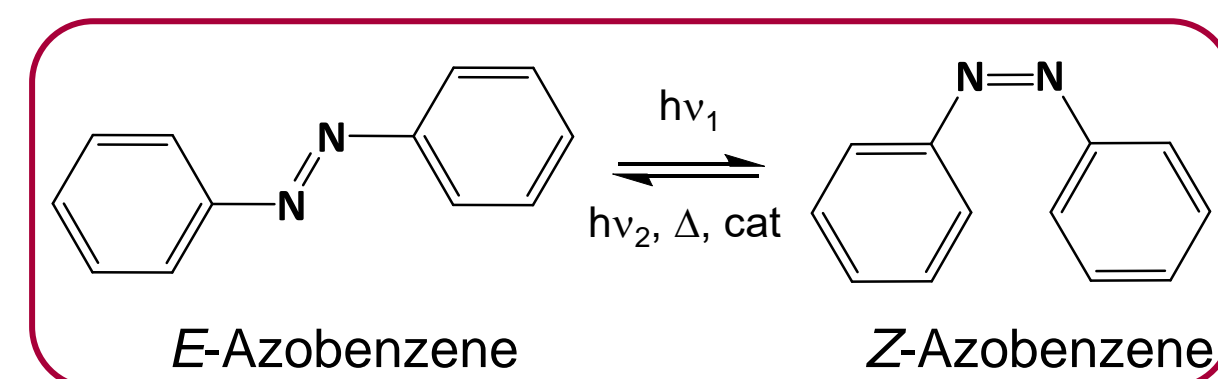


Figure 2: The isomerization reaction of azobenzene.

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 MOST 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 MOST properties.

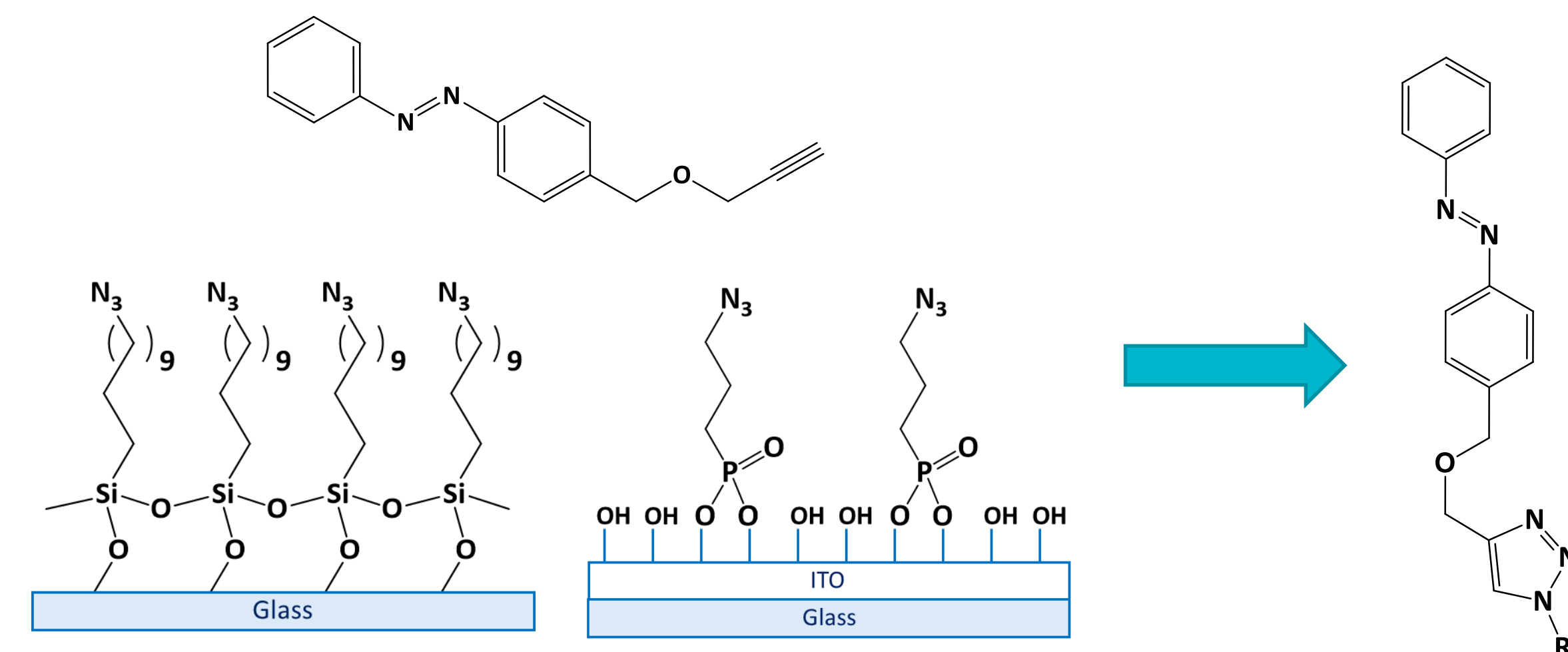
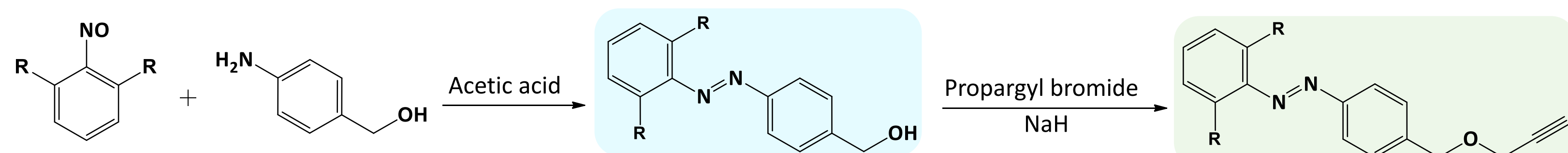


Figure 3: Azobenzene grafting on glass or ITO.

Synthetic procedure



Spectroscopic analyses : UV-Visible

UV-Vis spectra were recorded on a AvaSpec-2048 Fiber Optic Spectrometer. Azobenzene solutions ($C \approx 5 \cdot 10^{-5}$ M) were prepared in the dark at room temperature using HPLC grade acetonitrile as solvent. Three spectra were recorded : in the dark to prevent any photoisomerization, under UV light and under visible light.

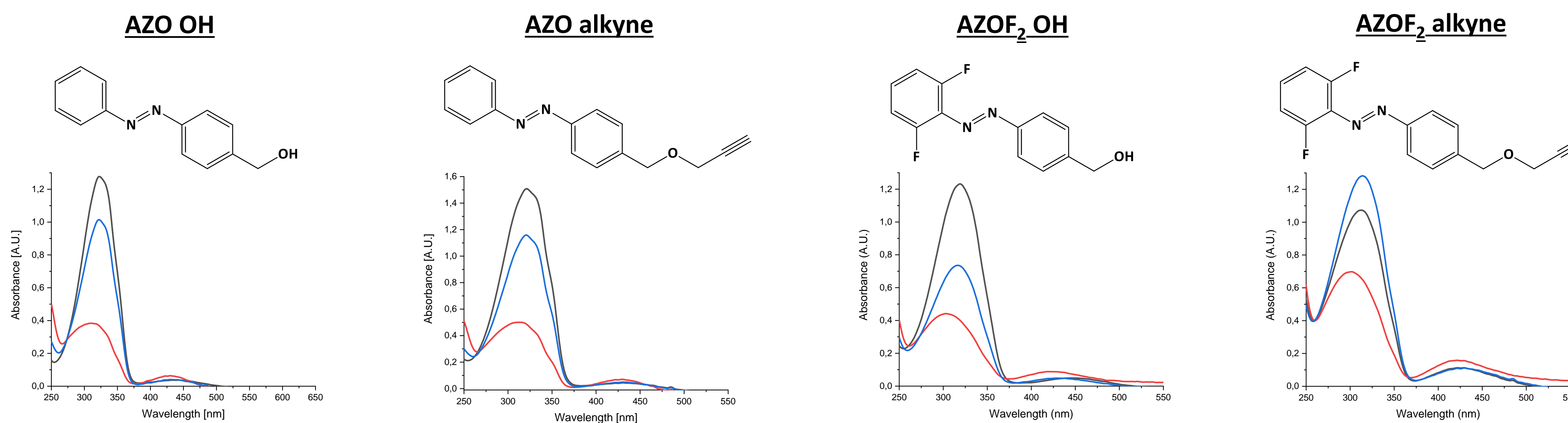


Figure 4: UV-vis spectra of AZO OH, AZO alkyne, AZOF₂ OH and the AZOF₂ alkyne with no irradiation (black line), vis-PSS (blue line) and UV-PSS (red line).

DARK	π - π^* (nm)	n - π^* (nm)
AZO OH	322	430
AZO alkyne	321	430
AZOF ₂ OH	318	445
AZOF ₂ alkyne	313	422

UV	π - π^* (nm)	n - π^* (nm)
AZO OH	312	430
AZO alkyne	312	430
AZOF ₂ OH	303	419
AZOF ₂ alkyne	300	422

Thermal back isomerization : LC-MS analyses

The AZO OH, AZO alkyne, AZOF₂ OH and the AZOF₂ alkyne in acetonitrile were irradiated with a lightningcure LC8 L9588-02A UV lamp (ca. 220 - 400 nm) for 2 minutes to induce isomerization. For the AZO OH and the AZO alkyne, the solutions were stored in the HPLC autosampler (in the dark, at a temperature of 40°C). For the AZOF₂ OH and the AZOF₂ alkyne, a stove was used to store the solutions at 70°C, in the dark. Liquid chromatography (Waters Alliance 2695) coupled to mass spectrometry (Waters QToF Premier, ESI (+)) 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 ($t_{1/2}$). Three replicates were done for each azobenzene and the average is in the table.

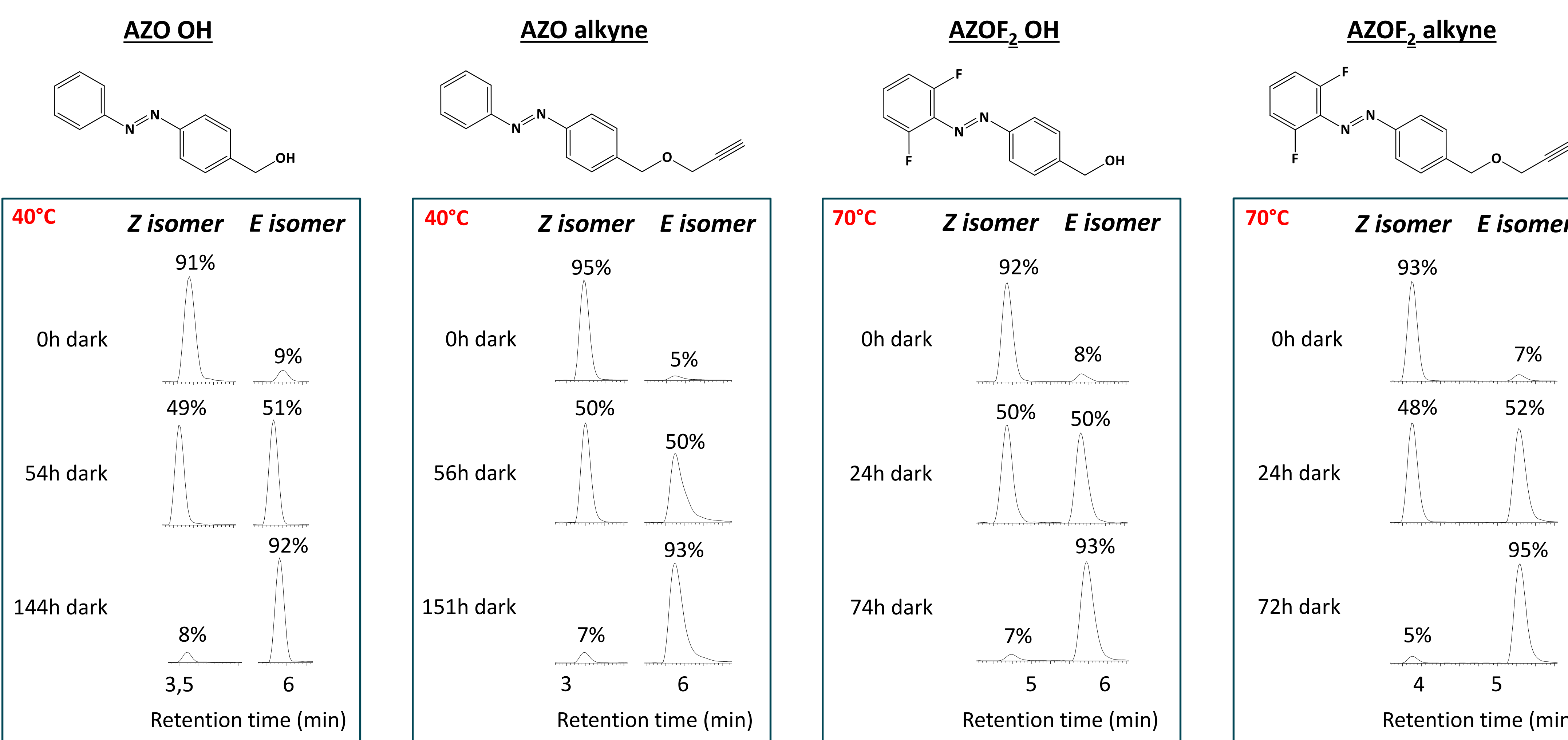


Figure 5: LC-MS analysis (Extracted Ion Current (EIC) chromatograms of the $[M+H]^+$ ions at m/z 213) for AZO OH.

Figure 6: LC-MS analysis (EIC chromatograms of the $[M+H]^+$ ions at m/z 251) for AZO alkyne.

Figure 7: LC-MS analysis (EIC chromatograms of the $[M+H]^+$ ions at m/z 249) for AZOF₂ OH.

Figure 8: LC-MS analysis (EIC chromatograms of the $[M+H]^+$ ions at m/z 287) for AZOF₂ alkyne.

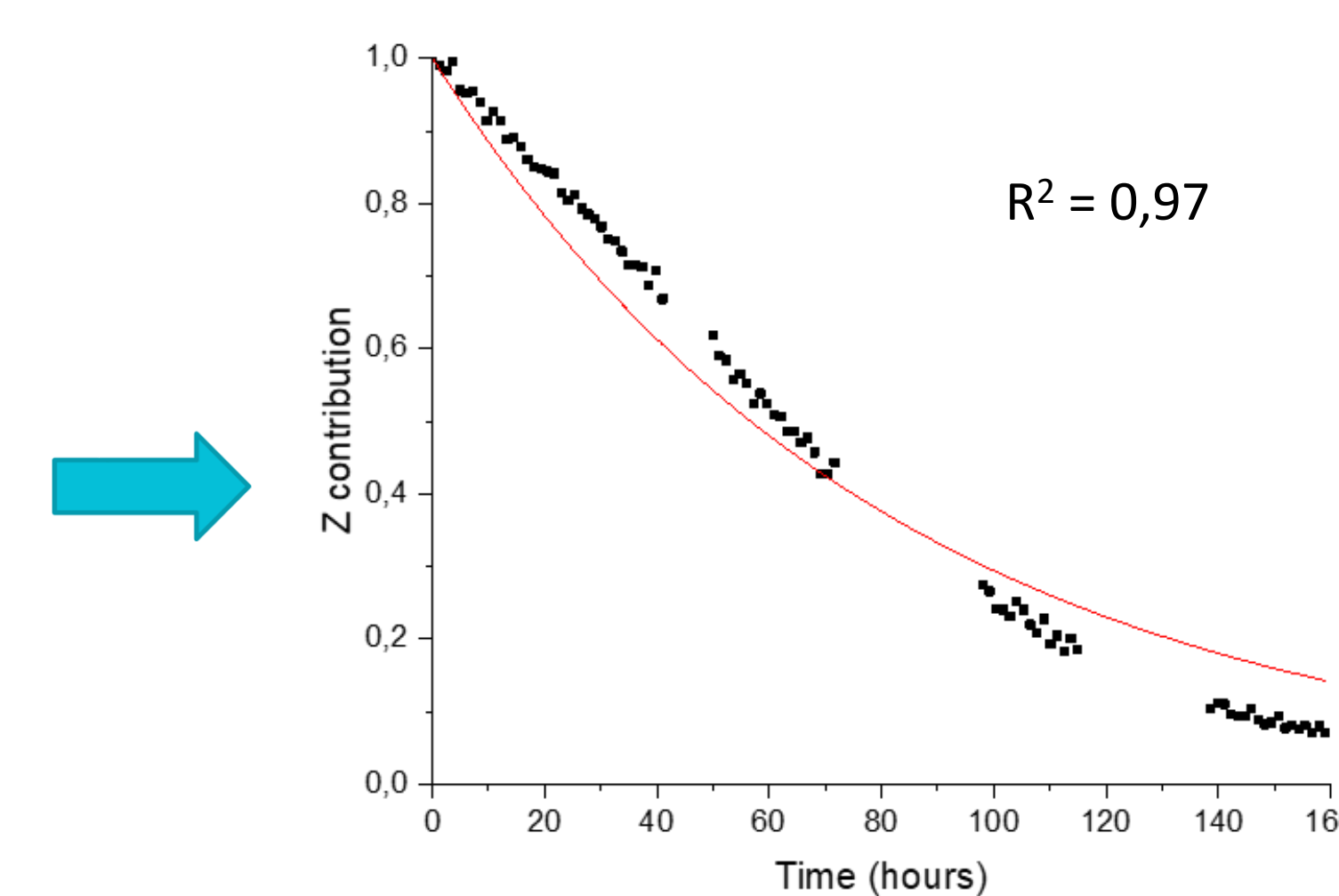


Figure 9: Plot of the Z isomer contribution for AZO alkyne as a function of time.

	k (10^{-3} h^{-1})	$t_{1/2}$ (h)
AZO OH	$13,0 \pm 0,2$	$53,3 \pm 1,0$
AZO alkyne	$12,5 \pm 0,3$	$55,5 \pm 1,3$
AZOF ₂ OH	$28,5 \pm 1,1$	$24,4 \pm 0,9$
AZOF ₂ alkyne	$30,0 \pm 0,5$	$23,1 \pm 0,4$

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

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 four azobenzenes. All the π - π^* bands and the n - π^* bands were measured in the UV and visible range, respectively. Based on LC-MS analyses, the half-lives of metastable AZO OH and AZO alkyne were about 13h and for the AZOF₂ OH and the AZOF₂ alkyne, 30h. This demonstrates that the terminal groups do not influence the properties, unlike the addition of fluorine atoms 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 MOST properties of these systems.

Acknowledgments

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