

# Self-Assembled Monolayers Based on Azobenzene Derivatives as Molecular Solar Thermal 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].

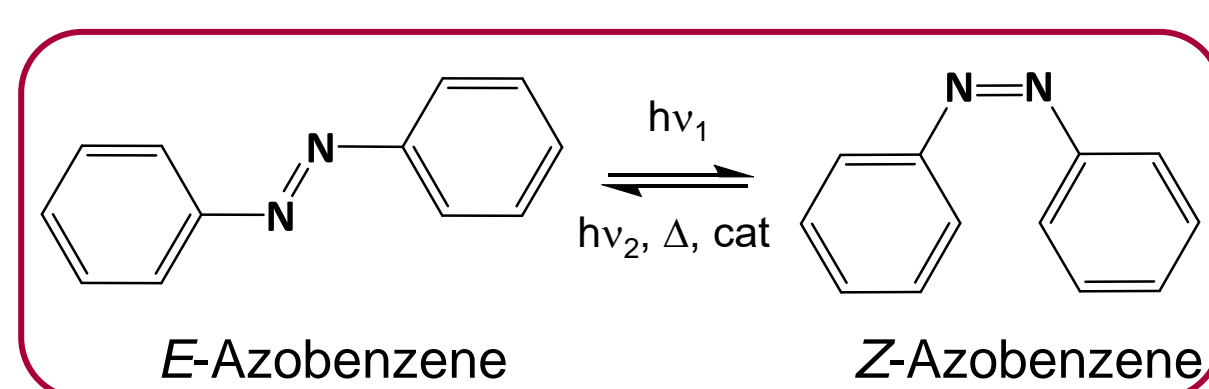


Figure 2: The isomerization reaction of azobenzene.

## Strategy of the study

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 phosphonic groups for their efficient chemisorption on metal oxides such as ITO (Indium-Tin-Oxide) [4]. The determination of the MOST properties of the isolated chromophores was performed before the SAM preparation to assess the impact of phosphonic acid group on the chromophore photoswitching properties and to further evaluate the role of intermolecular interactions within the close-packed assemblies on the MOST properties.

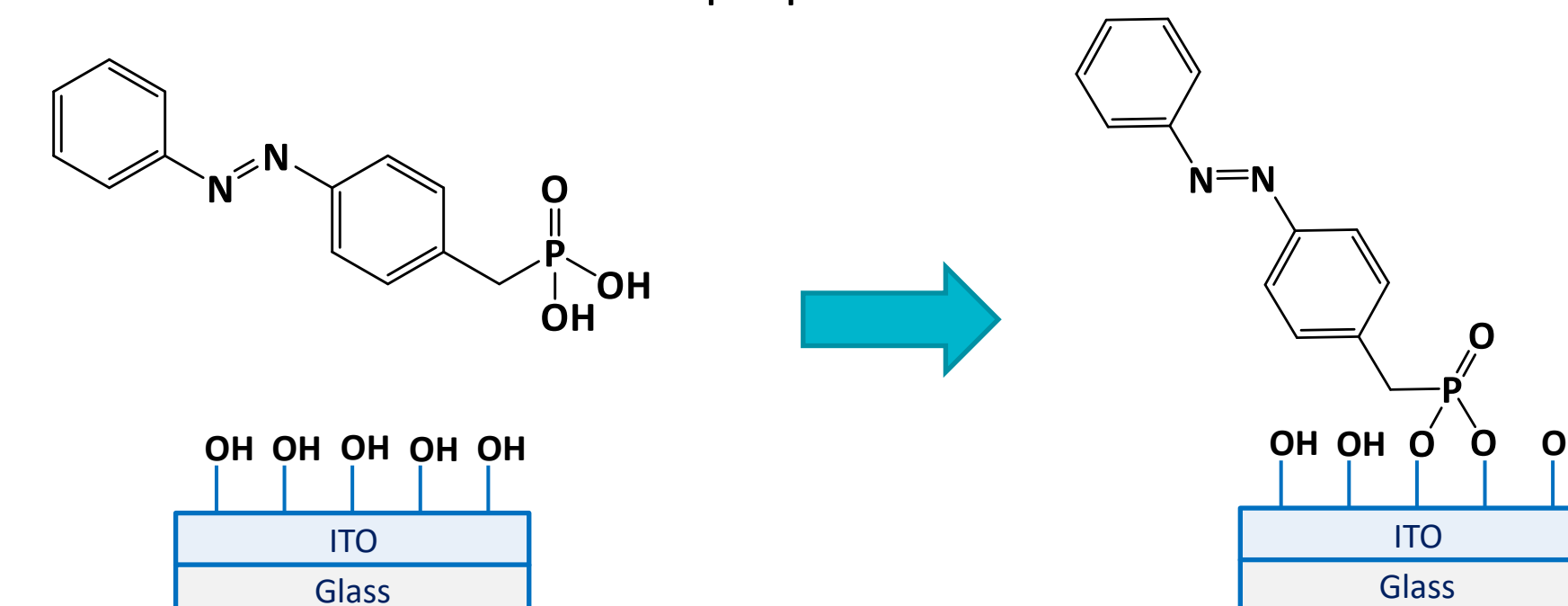


Figure 3: Azobenzene grafting on ITO.

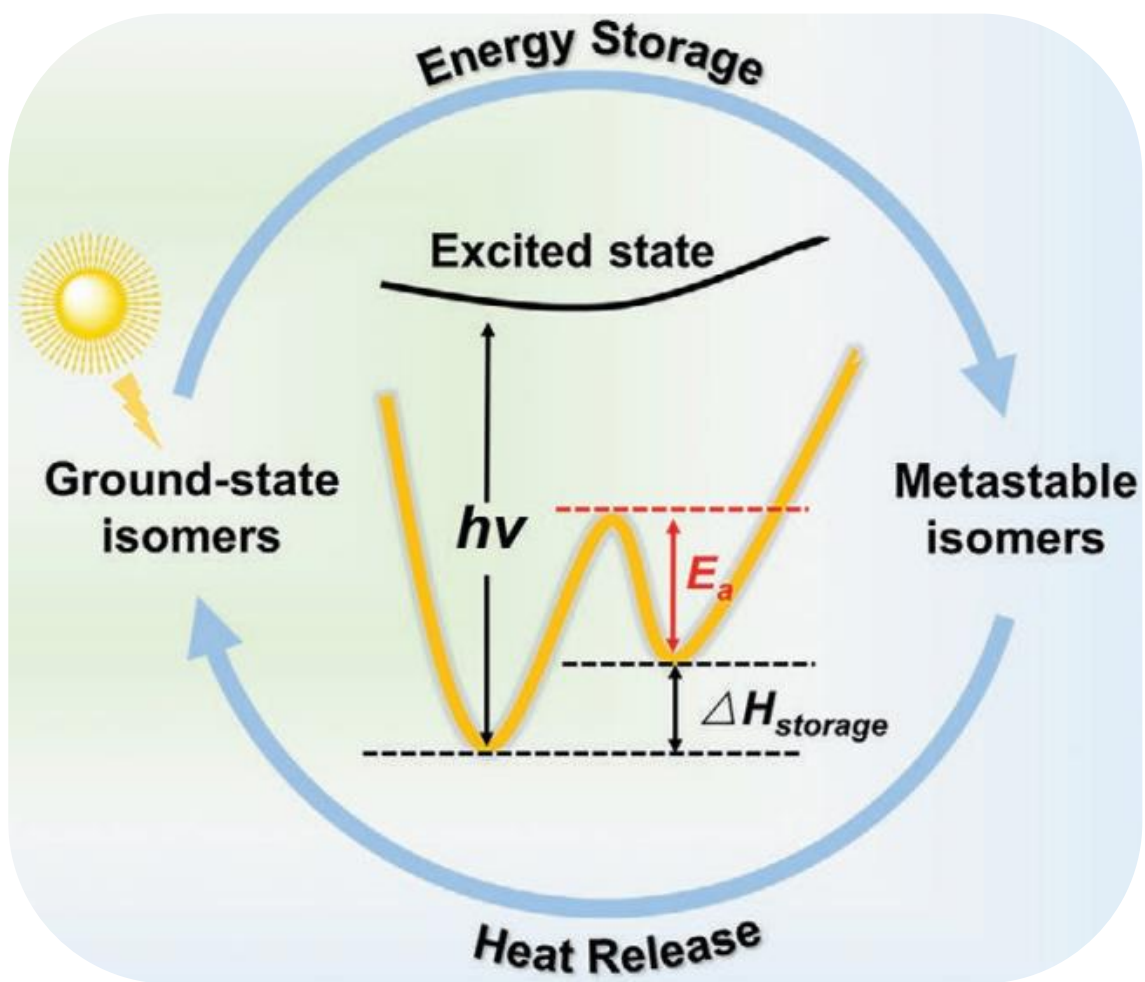
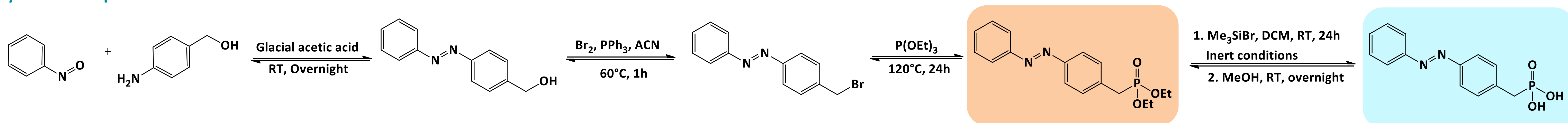


Figure 1: The solar thermal conversion of molecular photoswitches and their storage mechanism [1].

## Synthetic procedure



## Spectroscopic analyses : UV-Visible

UV-vis spectra were recorded on a AvaSpec-2048 Fiber Optic Spectrometer. Azobenzene solutions ( $C \approx 5.10^{-5}$  M) were prepared in the dark at room temperature using HPLC grade methanol as solvent. Three spectra were recorded : in the dark to prevent any photoisomerization, under UV light and under visible light.

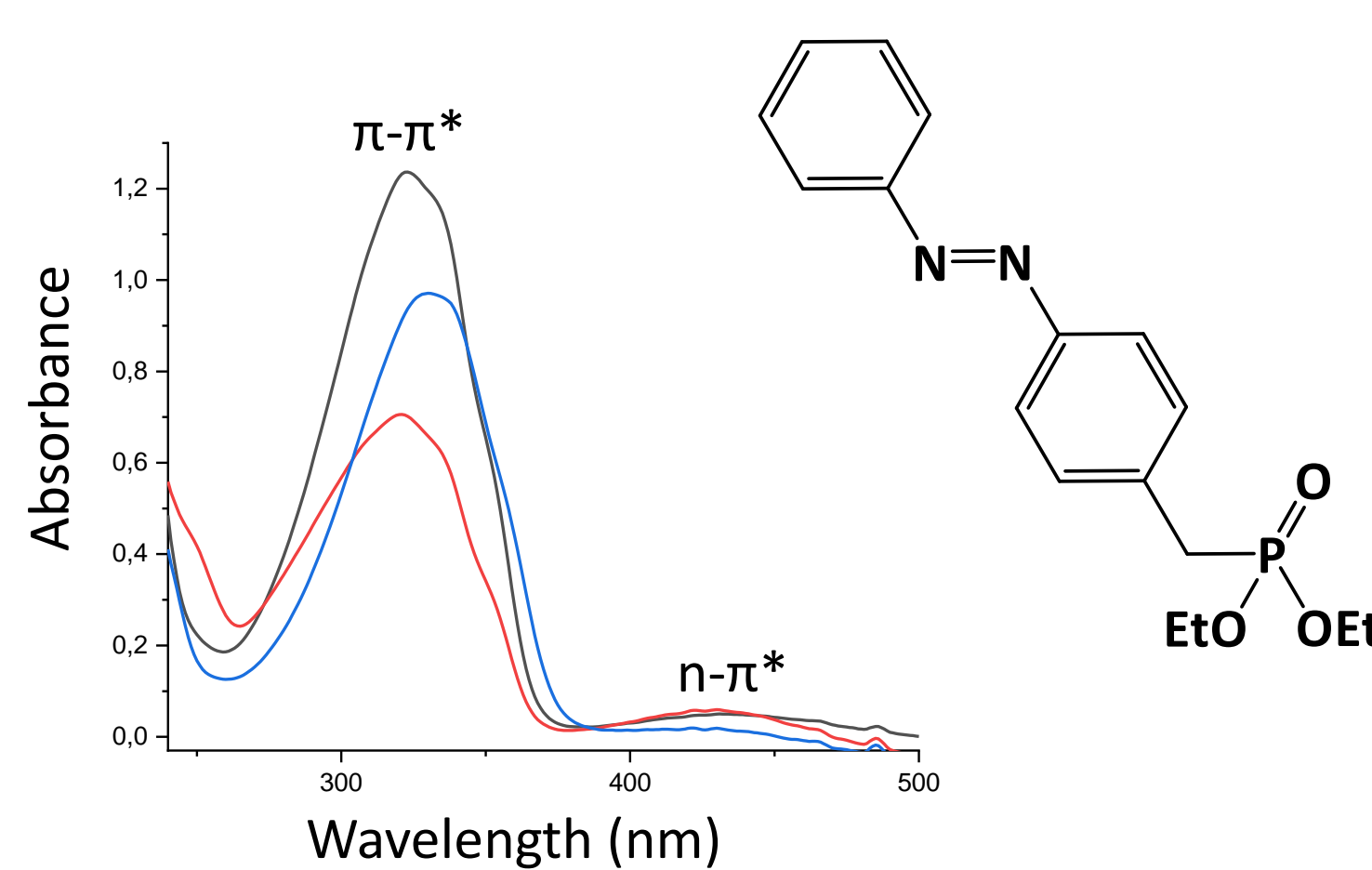


Figure 4: UV-vis spectra of AZO-PO<sub>3</sub>Et<sub>2</sub> with no irradiation (black line), vis-PSS (blue line) and UV-PSS (red line).

	$\pi$ - $\pi^*$ (nm)	$n$ - $\pi^*$ (nm)
AZO <sup>2</sup>	320	440
AZO-PO <sub>3</sub> Et <sub>2</sub>	323	430
AZO-PO <sub>3</sub> H <sub>2</sub>	322	430

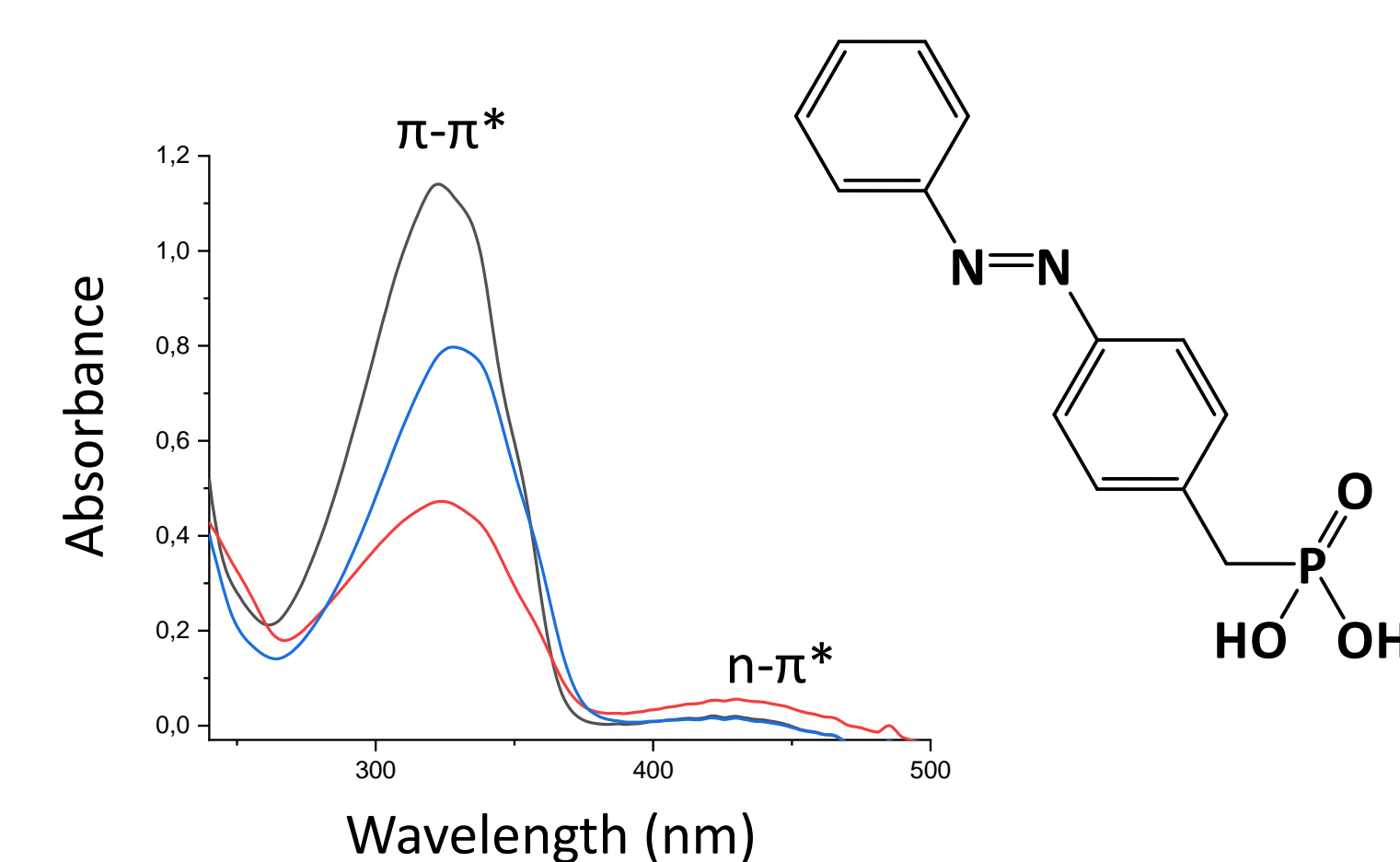


Figure 5: UV-vis spectra of AZO-PO<sub>3</sub>H<sub>2</sub> with no irradiation (black line), vis-PSS (blue line) and UV-PSS (red line).

## Thermal back isomerization : LC-MS analyses

The AZO-PO<sub>3</sub>Et<sub>2</sub> and the AZO-PO<sub>3</sub>H<sub>2</sub> in methanol were irradiated with a lightningcure LC8 L9588-02A UV lamp (ca. 220 - 400 nm) for 1 minute to induce isomerization. Then, the solutions were stored in the HPLC autosampler (in the dark, at a temperature of 40°C). Liquid chromatography (Waters Alliance 2695) coupled to mass spectrometry (Waters QToF Premier, ESI (+)) analysis 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.

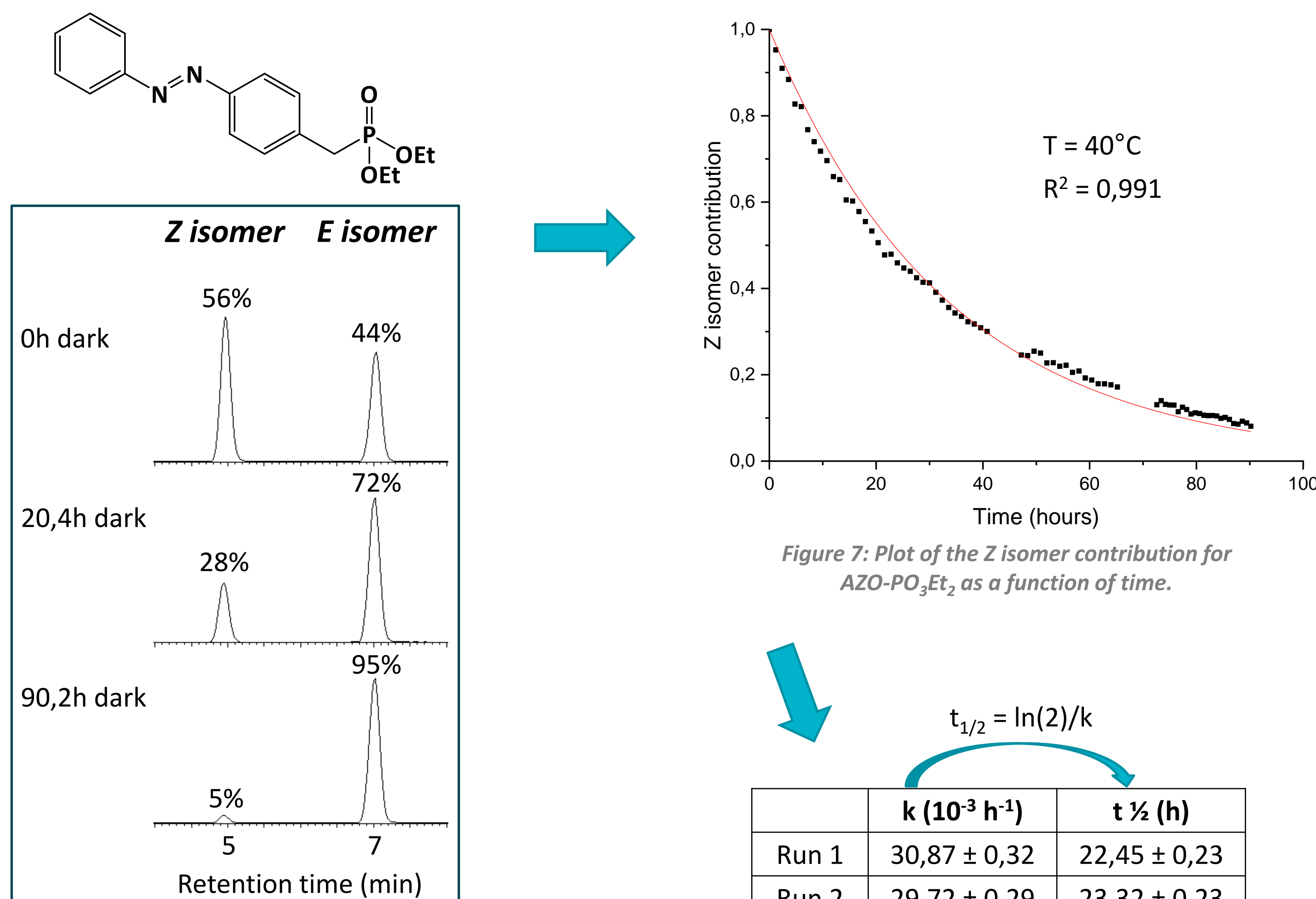


Figure 7: Plot of the Z isomer contribution for AZO-PO<sub>3</sub>Et<sub>2</sub> as a function of time.

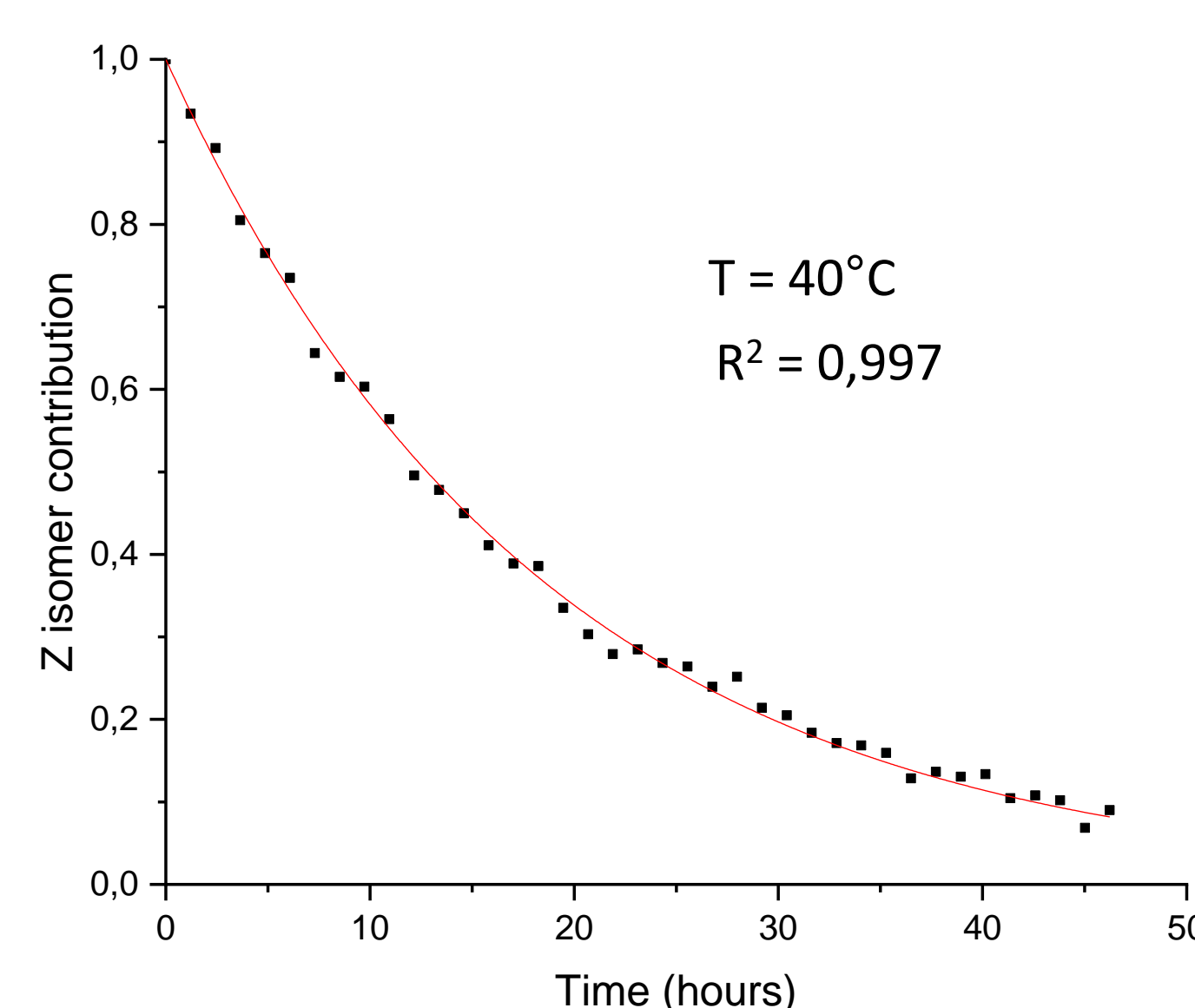


Figure 9: Plot of the Z isomer contribution for AZO-PO<sub>3</sub>H<sub>2</sub> as a function of time.

Figure 6: LC-MS analysis (Extracted Ion Current (EIC) chromatograms of the  $[M+H]^+$  ions at  $m/z$  333) for AZO-PO<sub>3</sub>Et<sub>2</sub>.

Figure 8: LC-MS analysis (Extracted Ion Current (EIC) chromatograms of the  $[M+H]^+$  ions at  $m/z$  277) for AZO-PO<sub>3</sub>H<sub>2</sub>.

## Conclusions

In this work, we prepared an azobenzene derivative bearing a phosphonic acid group for grafting onto ITO or glass. We carried out analyses on AZO-PO<sub>3</sub>Et<sub>2</sub> and AZO-PO<sub>3</sub>H<sub>2</sub>. Both the  $\pi$ - $\pi^*$  band and the  $n$ - $\pi^*$  band were in the UV and visible range respectively. Based on LC-MS analyses, the half-lives of metastable AZO-PO<sub>3</sub>Et<sub>2</sub> and AZO-PO<sub>3</sub>H<sub>2</sub> were determined ca. 23h and 13h. Theoretical calculations are in progress to understand the underlying substituent effect. 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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## References

- [1] X. Xu and G. Wang, *Small*, vol. 18, no. 16, **2022**
- [2] H. M. D. Bandara and S. C. Burdette, *Chem. Soc. Rev.*, vol. 41, no. 5, pp. 1809–1825, **2012**
- [3] N. Crivillers *et al.*, *Physical Chemistry Chemical Physics*, vol. 13, no. 32, p. 14302, **2011**
- [4] M. Han, D. Ishikawa, T. Honda, E. Ito, and M. Hara, *Chemical Communications*, vol. 46, no. 20, p. 3598, **2010**