



Tuning of the properties of rhodopsin-based molecular switches



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ABSTRACT

The modification of relevant chemical properties of rhodopsin-based molecular photoswitches is presented. We show how both the substituents present and the nitrogen atom quaternization are capable to change the wavelength of absorption and the thermal stability of the photoisomer. Adjusting these properties, the molecular switches could be turned into useful compounds for solar energy storage devices.

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Introduction

In recent years, the use of molecular switches to control diverse properties has become increasingly popular.^{1,2} Among the different types of reported switches, photoswitches have received considerable attention due to practical advantages such as high temporal and spatial resolution and lack of wastage products.³ Also, molecular photoswitches can be subsequently divided into two main classes: switches based on cyclization and *E/Z* isomerization. Fulgides,⁴ diarylethenes,⁵ spiropyran compounds⁶ and dihydroazulenes² are molecular switches based on photocyclization processes, while azobenzenes, overcrowded alkenes and retinal-based switches are based on photoisomerizations.⁷ The use of these and other molecular photoswitches has led to a number of amazing applications of the photocontrol of different properties from polymers^{8,9} to liquid crystals¹⁰ or peptide conformations.¹¹ Most of these applications rely on the use of light to interconvert the system between two different states, although usually some thermal reversion can also take place at different temperatures. Thus, the uses of switches in applications that need the photoisomer to be stable require higher temperatures to revert the isomerization. Additionally, the two isomers may not be isoenergetic and the temperature for interconversion may prevent or, at least, hamper the back-reaction under certain conditions. If this can be achieved, the switch could be used not only to affect a complex system, but also to provide a potential use in its own as energy storage. Specifically, the energy of a photon could be absorbed and stored in a

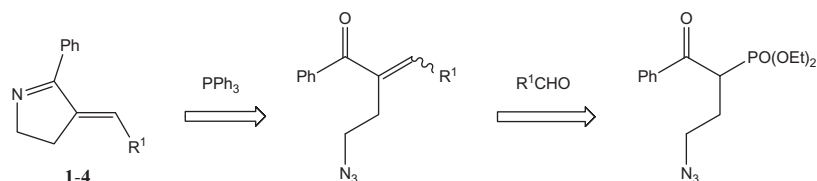
molecular photoswitch and the difference in energy between the two states could be released once an energy barrier for the back-reaction is surmounted. If the absorbed light is solar energy, the switch turns into a solar energy storage device. This concept is called Molecular Solar Thermal system (MOST) and it has gained some attention in the last years as an alternative to other energy conversion systems due to its functioning as a closed cycle and lack of emissions.¹² Stilbene-like molecules,¹³ fulvalene ruthenium complexes,¹⁴ and norbornadienes¹⁵ have already been explored as MOST energy storages.

We have been involved in a long term effort to design,^{16,17} synthesize^{18–21} and characterize²² diverse molecular photoswitches. Herein we report how a well-known type of molecular switch could be tuned to act as a part of a MOST system. Specifically, we prepared diverse derivatives of a rhodopsin-based molecular photoswitch in order to adjust their properties.

We based our study on the methylated and protonated versions of the previously reported rhodopsin-based molecular switches **1–4** (Scheme 1).¹⁹ These compounds were prepared through an expedient and versatile synthetic route. In all cases, the *E* isomer was found to be the more stable isomer. Irradiation of the switches between 1 and 3 h at 270–300 nm produced the photoisomerization under the reaction conditions (immersion well, medium-pressure Hg lamp, Pyrex filter). Also, the photoswitches could be reset after heating. These features turned the rhodopsin-based compounds into promising candidates for their use as photoswitches in diverse applications. Taking these compounds as starting points, we tried to modify the properties of these molecules to explore the possibility to turn them into potential candidates for MOST systems. To do this, the features required to

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Scheme 1. Retrosynthesis of rhodopsin-based photoswitches.

be changed are the wavelength of absorption and the thermal stability. First, in order to act as a MOST system, the chromophore should absorb substantially in the visible region of the spectrum. Second, the back-reaction should take place only when needed and thus, thermal relaxation should be minimized at low temperatures. These two modifications were addressed separately. Also, the kinetics of photoisomerization for the derivatives were assessed. Additionally, theoretical calculations were performed in order to provide the required background for further development.

Results and discussion

Two main modifications were considered in order to prepare derivatives suitable for acting as MOST systems, R^1 substitution and nitrogen atom quaternization. Modification of the substituent present in R^1 has been shown to have an effect on different properties of these molecules acting as molecular switches, as the Photostationary State (PSS) and the thermal stability. However, the influence of R^1 on the wavelength of absorption is small.¹⁹ On the other hand, it is well-known the influence of the quaternization on the photophysics of the rhodopsin and rhodopsin-based molecules.²³ A red-shift of the absorption band is usually found when comparing the quaternized salts with the neutral analogues. Thus, we explored these two types of modifications in order to tune the properties of these molecules to match the MOST system requirements.

Starting from the neutral molecular switches previously synthesized,¹⁹ we prepared new compounds by quaternization of the nitrogen atom of the imine bond. To this purpose, protonation or methylation of diverse compounds with substituents of the aromatic ring with different electronic properties was carried out by adding one equivalent of tetrafluoroboric acid (HBF_4) or methyl triflate ($\text{CF}_3\text{SO}_3\text{CH}_3$). For the methylated analogues **5–8**, after the addition of the triflate in dry toluene, the iminium salt precipitates and can be easily isolated from the filtrate. For the protonated derivatives **9–11**, the addition of one equivalent of acid led to the quantitative formation of the salt as determined by ^1H NMR. In this case, the use of different acids such as triflic acid ($\text{CF}_3\text{SO}_3\text{H}$) or HCl causes an analogous effect as previously shown in similar compounds.²¹ Results are shown in Chart 1 and Table 1.

Prior to the irradiation of these methylated and protonated compounds, their UV–vis spectra were recorded to compare the results obtained to the UV–vis spectra of the neutral compounds. Therefore, we prepared 10^{-5} M solutions of compounds **5–8** in

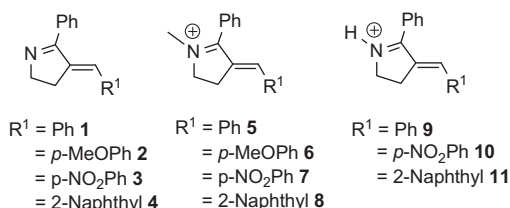


Chart 1. Studied compounds.

Table 1
Synthesized methylated derivatives^a

Neutral compound	R_1	Derivative	Yield (%)
1	Ph	5	95
2	<i>p</i> -MeOPh	6	90
3	<i>p</i> -NO ₂ Ph	7	97
4	2-Naphthyl	8	85

^a Protonated derivatives **9–11** were formed quantitatively.

acetonitrile. The obtained spectra for each compound were plotted in the same graph as the spectrum of their corresponding neutral compound. In Figure 1, the UV–vis spectra of compounds **1** and **5** are represented. As can be seen, a bathochromic shift of the maximum of the absorption band ($\Delta\lambda_{\text{max}} = 45$ nm) when methylating **1** is observed. Similar results were obtained for **2–4** and their methylated analogues **6–8** (see Supplementary material). Interestingly, the protonated derivatives **9–11** share all the features with the methylated compounds. This implies that the quaternization of the switches yields different compounds, under different reaction conditions but with the same properties. In turn, this would be of practical importance for the implementation of these compounds as applied systems.

After analysing the UV–vis spectra of the quaternized analogues, we proceeded to irradiate them. To compare the isomerization process of the neutral and methylated compounds, similar graphs were obtained for the isomerization of the neutral and methylated compounds. The results obtained are summarized in the following Table 2 (see Supplementary material). Again, the protonated compounds **9–11** yielded a PSS with the same composition than the methylated analogues.

From these results, we can deduce that in all cases the percentage of the *Z* isomer (photochemically obtained isomer) at the PSS is higher when the compounds are in their neutral form than when

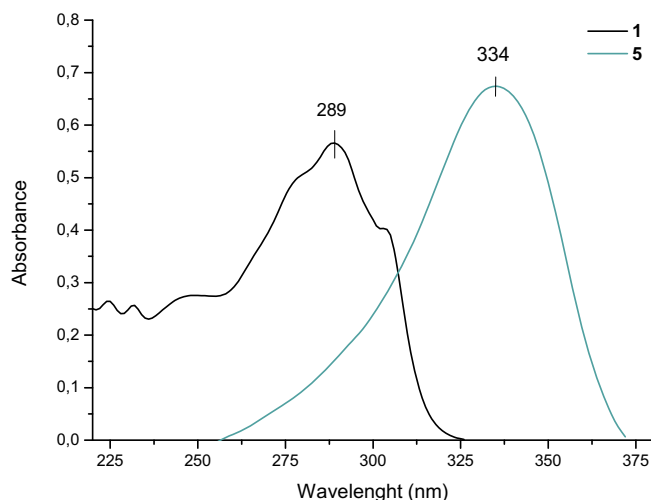


Figure 1. UV–vis spectra of **1** and **5** in acetonitrile.

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