

Reversible C=N Bond Formation Controls Charge-Separation in an Aza-Diarylethene Photoswitch

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Abstract

Diarylethene belong to the most eminent photoswitches and have been studied for many decades. They are found in virtually every field of applications and have become highly valuable molecular tools for instilling light-responsiveness into materials, catalysts, biological systems, or pharmacology. In this work we present a novel and distinct type of pyrimidine-based aza-diarylethene, which undergoes a highly unusual zwitterion-forming photoreaction. During this fully reversible process a CN double bond is established under concomitant aromatization and thiophene-ring opening. The metastable zwitterion thus possesses a positively charged extended aromatic structure and an appendant conjugated thiolate function. It can further photoisomerize between a more stable *Z* and a less stable *E* isomer, resulting in effective three-state photoswitching. Unusual for diarylethenes, the metastable isomers show negative solvatochromism and redshifted absorption in apolar solvents. Thermal stability of the zwitterions can be modulated from a dissipative to a highly stable behavior in response to pH, again in a fully reversible manner. Pyrimidine-based aza-diarylethene thus establishes a unique photoreaction mechanism for diarylethenes allowing to control charge separation, thermal stability, and color generation in a different way than hitherto possible.

Introduction

Molecular photoswitches enable the translation of light energy into predictable molecular changes and therefore offer precise control over the states of matter and its behavior at the smallest scales.^{1, 2} The field of molecular photoswitch research has grown immensely in the last decades and in addition to more traditional motives like stilbenes,^{3, 4} azobenzenes,⁵ or

diarylethenes,⁶⁻⁸ new motives, e.g. hydrazones,⁹ Stenhouse dyes,^{10, 11} imidazole-biradicals,^{12, 13} or indigoids¹⁴⁻¹⁶ have been developed more recently. In addition to this increasing diversification, classical photoswitches like azobenzenes¹⁷⁻²² and diarylethenes^{6, 23-26} have been subject to steep developments themselves and are found in virtually every application driven field of chemical research. With the advent of facile synthetic access to nonsymmetric diarylethenes²⁷⁻²⁹ new and exciting opportunities have emerged for structural-functional diversification and unique applications of this class of photoswitches, e.g. in catalysis,³⁰ dynamic covalent chemistry,³¹ molecular logic,³² chemical biology,³³⁻³⁵ or materials research.³⁶ To our surprise however, no investigations had been made to examine the possibility of forming and breaking CN bonds during the electrocyclic photoreaction in diarylethenes when we started this investigation. Just very recently, the group of Kobatake has published the reversible C-N single bond formation in a two-state aza-diarylethene photoswitch, similar to the C-C bond electrocyclization reactions observed in the parent compound.³⁷

In this work we disseminate the reversible C=N double bond formation and breaking of pyrimidine-substituted three-state aza-diarylethene photoswitch, which proceeds via a concomitant thiophene-ring opening and formation of an aromatized zwitterionic metastable state. The metastable state is strongly colored and fully reverts back to the colorless open ring aza-diarylethene. Because of the zwitterionic character in the ground state, the closed ring isomer shows a rare negative solvatochromism with red-shifted absorption in apolar solvents and blue-shifted absorption in polar media. The thermal stability of the metastable state is highly sensitive to pH and can be modulated from a dissipative behavior to a highly thermally stable one. This very unusual photoswitching mechanism and the resulting facile pH control over the T-type photochromism will open up exciting realms of applications for pyrimidine-diarylethenes in e.g. sensing, materials, or biological research in the future.

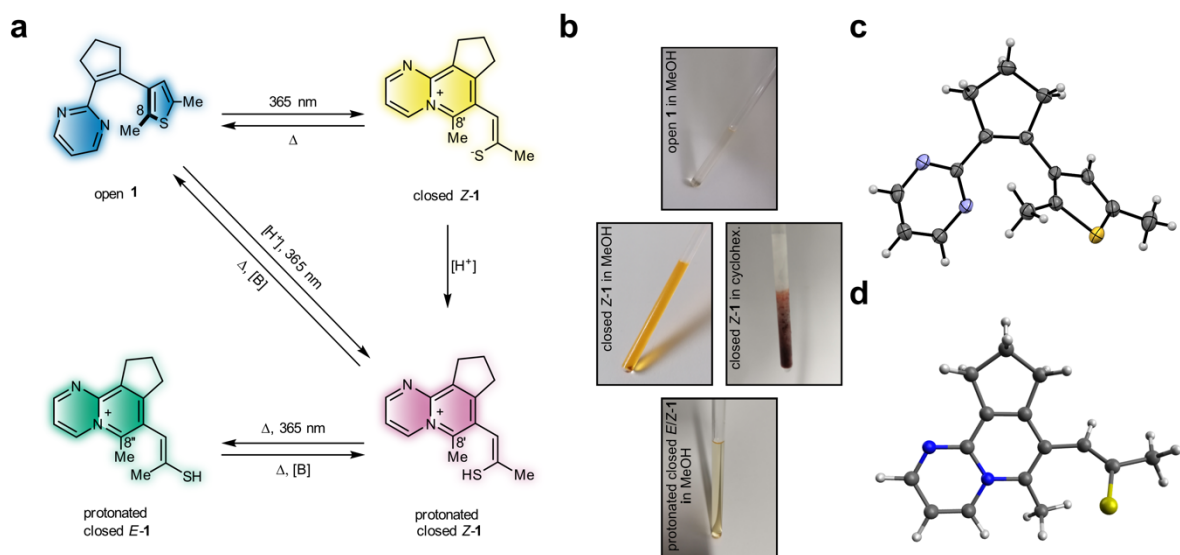


Figure 1 a Non-symmetric pyrimidine based diarylethene (**1**) with photo-, pH-, and thermal switchability between open **1** (blue), closed **Z-1** (yellow), protonated closed **Z-1** (magenta) and protonated closed **E-1** (green). b Photographs of open **1** in MeOH solution (top), closed **Z-1** in MeOH solution (middle left), in cyclohexane solution at $-78\text{ }^{\circ}\text{C}$ (middle right), and protonated closed **Z-1** in MeOH solution (bottom). c Structure of open **1** in the crystalline state as determined by X-ray diffraction. d Structure of closed **Z-1** optimized at the TPSS0-D3BJ/def2-TZVPP-CPCM(MeOH) level of theory.

Results and Discussion

Synthesis of open **1** follows the literature known synthesis route that has been published by the group of Feringa,²⁸ and then been adapted by the group of Jäschke.³⁴ This synthesis route has allowed the non-symmetric substitution of diarylethene photoswitches, and therefore opened up a new plethora of structures. To allow the synthesis of non-symmetric pyrimidine diarylethenes, the three main components (two substituents and the central cyclopentene core) were synthesized separately and combined via Suzuki-Miyaura cross coupling reactions. First, 2,5-dimethylthiophene (**2**) was brominated via *N*-bromosuccinimide (NBS) to form 4-bromo-2,5-dimethylthiophene (**3**, 93%). The central core 1,2-dibromocyclopentene (**4**, 51%), was obtained from cyclopentanone via bromination with elemental bromine in the presence of PCl_5 and elimination of POCl_3 after base treatment. After a halogen-lithium exchange at **3** and conversion to the respective boronic acid, the species was cross coupled with **4** in situ to obtain precursor 3-(2-bromocyclopent-1-en-1-yl)-2,5-dimethylthiophene (**5**, 86%). To avoid synthesis of a symmetric photoswitch via twofold cross coupling at this crucial reaction step,

4.0 equiv. of **4**, and 1.0 equiv. of **3** had to be used. **5** was again treated with *n*BuLi and a dioxaborolane to synthesize the pinacol protected precursor 2-(2-(2,5-dimethylthiophen-3-yl)cyclopent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6**, 71%), which can then undergo cross coupling with 2-iodopyrimidine to yield the final product of open **1** (73%). Crystals suitable for structural analysis were obtained for open **1** confirming the connectivity and open ring constitution (Figure 1c).

Open **1** possesses absorption in the UV range and therefore was irradiated with 285 nm or 365 nm light (Figure 2). Unexpectedly, we did not observe the photoproduct of a classical 6π -electrocyclic diarylethene reaction, which was recently reported to take place in thiazole-diarylethene.³⁷ Instead, irradiation leads to the electrocyclic formation of a positively charged aromatic pyrido[1,2-*a*]pyrimidin-5-ium ring in conjunction with reversible C-S bond breaking and ring opening of the adjacent thiophene. Overall, a zwitterionic thiolate species is obtained in up to 94% yield (Figure 1a, 1c, 2c), which is colored and shows rare negative solvatochromism, typical for charged ground state species. This unusual C=N bond forming photoreaction was elucidated fully by a comprehensive UV/Vis and NMR analysis in solution (Supporting Information and Supporting Figures 12-21) in conjunction with theoretical modeling at the TPSS0-D3BJ/def2-TZVPP-CPCM level of theory (see Supporting Information for details). Only one signal set of a closed **1** species is observed in the NMR experiments in MeOH solution, which matches well with the theoretically predicted and significantly more stable *Z* isomeric thiolate. It does not match at all with the theoretical predictions for the conventional 6π -electrocyclization product. In the following, key-observations of this analysis are highlighted. A ¹H-¹⁵N HMBC NMR experiment directly established covalent bond connectivity between C8' of the former thiophene ring (C8) with one pyrimidine nitrogen atom via cross signals to the adjacent methyl protons. The observed aromatic chemical shift of the particular carbon C8' within the newly formed C=N bond corresponds to a charged iminium species, which is fully supported by the theoretical calculations. In case of a conventional 6π -electrocyclization product, the C8' would possess aminothioliol character with a distinct aliphatic chemical shift, which is not observed. Further HMBC and NOE experiments as well as chemical shift comparisons between experiment and theory fully support the zwitterionic character and *Z* configuration of the closed **1** species (see Supporting Information for the full analysis).

Return of the closed *Z-1* species to the thermodynamically most stable open **1** via closing the thiophene ring and opening the C=N bond occurs spontaneously in methanol at 0 °C in the dark with a corresponding *Gibbs* energy of activation of 20.4 kcal mol⁻¹ (Figure 2a). This behavior establishes fully reversible photoswitching of aza-diarylethene **1** in high yields for both switching states.

When enriching closed *Z-1* in MeOH solution by UV light irradiation, the corresponding UV/Vis spectral changes are very similar to those of conventional ring-closed diarylethenes with a broad absorbance band emerging in the visible range between 400 nm – 500 nm (Figure 3a). The theoretically obtained UV/Vis spectra of open **1** and closed *Z-1* in MeOH are shown in Figure 3b. A good match between experimental and theoretical absorption spectra were obtained when four explicit MeOH solvent molecules in proximity to the thiolate moiety were included in the calculations, which shows a significant influence of the surrounding medium (see Supporting Information and Supporting Figure 96 and 97). In MeOH solution, open **1** appears as colorless solution while the closed *Z-1* species is colored orange (Figure 1b and Supporting Figure 61). Because of the particular *Gibbs* energy of activation for thermal reversion to open **1** a dissipative behavior can be established. Thereby, continued irradiation allows to color the solution while quick reversion to colorless occurs upon removal of the irradiation source (Supporting Video 1). When moving to cyclohexane as a very apolar solvent, the closed *Z-1* species could be observed in a deep red color after irradiation but only upon freezing the solvent to at least –78 °C (Figure 1b, Supporting Video 2, Supporting Figure 22, Supporting Figure 60). This behavior establishes a drastically reduced thermal stability of the closed *Z-1* species in an apolar environment. The strong negative solvatochromism evidences severe excited state stabilization and/or ground state destabilization leading to a bathochromic absorption shift in apolar solvents. Both observations further support the zwitterionic character of the metastable closed **1** isomer.

After establishment of the unexpected photoswitching behavior of aza-diarylethene **1** we investigated its behavior in the presence of pH changes. First, a sample of open **1** was dissolved in a mixture of MeOD-*d*₄ and 10 equiv. TFA-*d*₁ and irradiated with 365 nm light at 0 °C within the NMR spectrometer (Figure 2d, Supporting Figure 25). A distinct sequential isomer interconversion was observed. First, direct formation of closed *Z-1* is observed until it dominates the mixture almost completely. Only afterwards the signals of closed *E-1* are starting to increase. Thus, the photoreaction of open **1** in acidic conditions leads exclusively to

formation of closed **Z-1**, which is expected because of the *Z* configured double bond within the thiophene ring. Only after significant amounts of closed **Z-1** are formed a second photoequilibrium is entered leading to closed **E-1** accumulation. By timing the irradiation it is thus possible to either obtain closed **Z-1** almost quantitatively or arrive at a 1:1 mixture of closed **Z-1** and closed **E-1** (Figure 2d, 2e). Irradiation at $-40\text{ }^{\circ}\text{C}$ (Supporting Figure 30) gave the very same result fully excluding interference of thermal reactions with the photoreactions (see Supporting Information for details).

Elucidation of the molecular structures as well as double bond configurations of protonated closed **Z-1** and protonated closed **E-1** was achieved again by a comprehensive NMR analysis (see Supporting Information for details). The key experiments for elucidating the double bond configurations are described in the following. A ^1H - ^{13}C HSQMBC experiment directly allowed measuring coupling constants for the enethiol fragments and assigning *E* and *Z* configurations. ^1H - ^1H NOE experiments in $\text{MeOD-}d_4/\text{TFA-}d_1$ and $\text{DMSO-}d_6/\text{TFA-}d_1$ solutions further supported *E* and *Z* configuration assignments for the two closed **1** isomers. 1D and 2D NMR experiments in $\text{DMSO-}d_6/\text{TFA-}d_1$ directly revealed the thiol proton signals. An additional experiment in $\text{DMSO-}d_6/\text{TFA-}d_1$ solution allowed to directly observe formation of a fourth species upon irradiation. This species could unambiguously be assigned to the closed **1** thioketone structure via its hallmark $\text{C8}''$ ^{13}C chemical shift of 255 ppm and corresponding cross signals with other nuclei (see Supporting Information for all details). Observation of the thioketone **1** further evidences the thiophene ring-opening, which is the prerequisite for a subsequent thioketone/enethiol equilibrium.³⁸

Annealing the **Z-1** / **E-1** isomer mixture in $\text{MeOD-}d_4/\text{TFA-}d_1$ to $50\text{ }^{\circ}\text{C}$ shows that the protonated closed **1** forms are now greatly stabilized and do not convert thermally to open **1** for several hours. Thus, a repeat of the irradiation experiment in $\text{MeOD-}d_4/\text{TFA-}d_1$ (10 equiv.) at $25\text{ }^{\circ}\text{C}$ was conducted (Figure 2e). At the higher temperature the same sequential behavior of first **Z-1** and then **E-1** accumulation was observed under irradiation. A final **E-1** : **Z-1** ratio of 48% : 52 % is established in the photostationary state (pss) and again a quantitative combined yield was achieved in the photoreaction (Figure 2e). Adding 20 equiv. Et_3N to the sample resulted in fast recovery of open **1** in up to 82% (Figure 2e, Supporting Figure 27). The significantly greater thermal stability of the protonated closed **Z-1**/**E-1** isomers at lower pH can straightforwardly be explained by protonation of the thiolate. The resulting thiol possesses a drastically reduced nucleophilicity and thus diminished capability for attacking carbon $\text{C8}'$ (Figure 1a),

closing the thiophene ring, and opening up the pyrido[1,2-a]pyrimidin-5-ium ring. The kinetics of thermal isomerizations of protonated closed *Z*-1 and *E*-1 were scrutinized by ¹H NMR spectroscopy at 50 °C in the dark (Figure 2b). The experimentally determined variation in isomer content over the course of the experiment was modeled using the COPASI tool. It was found that thermal isomerization from protonated closed *Z*-1 to open 1 proceeds fastest with an associated *Gibbs* energy of activation of $\Delta G^\ddagger = 25.6$ kcal mol⁻¹. The corresponding *Gibbs* energy of activation for isomerization from protonated closed *Z*-1 to protonated closed *E*-1 was determined to 26.2 kcal mol⁻¹, and for protonated closed *E*-1 to protonated closed *Z*-1 to 26.7 kcal mol⁻¹ (Supporting Figure S9).

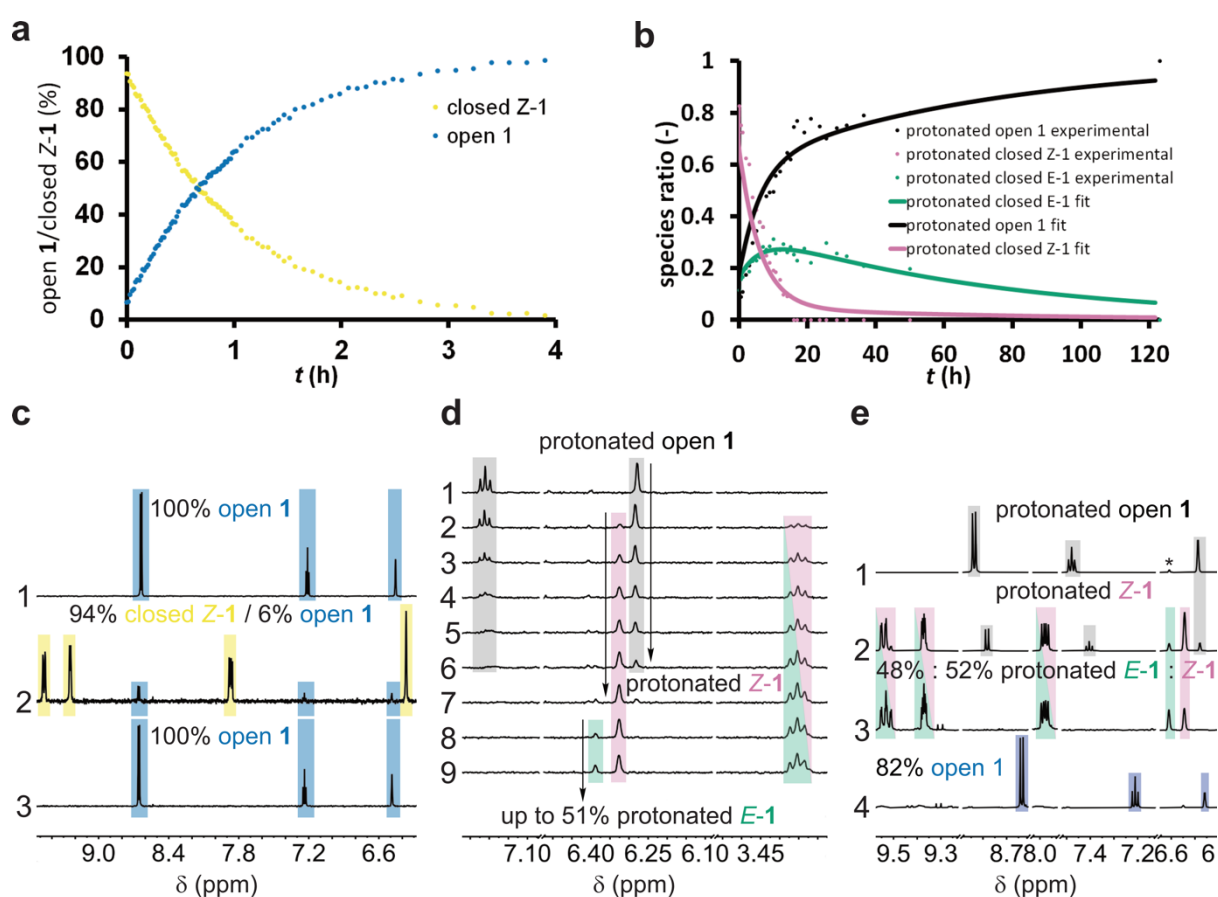


Figure 2 Thermal and photochemical behavior of aza-diarylethene 1. **a** Thermal conversion of closed *Z*-1 (yellow) to open 1 (blue) at 0 °C. **b** Thermal conversion of protonated closed *Z*-1 (magenta) and protonated closed *E*-1 (green) to open 1 (black) at 50 °C within 123 h. Experimental data (dots) were fitted by COPASI modelling (lines). **c** Partial ¹H NMR (401 MHz, MeOD-*d*₄, 0 °C) spectra of 1 before (1) and after (2) irradiation at -78 °C with 285 nm light, as well as after thermal reversion to open 1 in the dark (spectrum 3). **d** Partial ¹H NMR spectra (401 MHz, MeOD-*d*₄ + 10 equiv. TFA-*d*₁, 0 °C) of protonated 1 recorded before and after prolonged in situ irradiation with 365 nm light

at 0 °C. First protonated closed *Z-1* is formed (spectra 1-7, * impurity) and subsequently protonated closed *E-1* (spectra 7-9). e Partial ¹H NMR spectra (401 MHz, MeOD-*d*₄ + 10 equiv. TFA-*d*₁, 23 °C) of protonated **1** recorded before (spectrum 1) and after photoirradiation to pss with 365 nm light at 23 °C (spectra 2 to 3). 82% of open **1** can be recovered after addition of 20 equiv. Et₃N (spectrum 4).

Taken together, the strong and reversible pH responsiveness allows to convert photoswitch **1** from a dissipative system into a highly stable T-type photoswitch, altering the thermal isomerization half-life (Supporting Figure 56, Supporting Figure 58) from 1.6 min to 335 h at 25 °C (linearly extrapolated values from experimental data acquired at 0 °C and 50 °C). Protonation thus serves as a chemical lock to stabilize the metastable closed *E/Z-1* forms while at the same time reducing the nucleophilicity of the initially formed thiolate. The chemical locking process was further evidenced by starting with a solid probe of open **1**, which was irradiated with 365 nm light and subsequently dissolved in a mixture of MeOH/TFA (10 equiv.) leading to the thermally stable protonated closed **1**. Likewise, a MeOH solution of open **1** was irradiated and TFA (10 equiv.) was added directly afterwards to convert the system from dissipative into thermally stable in a sequential fashion (Supporting Video 3, Supporting Figure 62).

The photoreaction of open **1** in the presence of acid was further scrutinized with UV/Vis spectroscopy to gain further insights into the process (Figure 3c and 3d). Addition of TFA (up to 10 equiv.) has no significant influence on the absorption spectrum of the open **1** form. However, a significant effect is observed on the absorption of the closed **1** isomers, which lose their broad absorption band in the visible region of the spectrum upon addition of TFA. This behavior is in full accordance with protonation of the thiolate and a resulting dramatic decrease of its electron-donating capability. Overall, the push-pull character of the open **1** chromophore is therefore significantly reduced upon protonation, resulting in a strongly hypsochromically shifted absorption spectrum. Both closed isomers *Z-1* and *E-1* possess rather similar UV/Vis absorption spectra, which are very well reproduced in the theoretical description (Figure 3c and d). It should be noted that the initially expected closed-ring photoproduct typical for diarylethenes would not show such dramatic absorption shifts in response to protonation, which further supports our structural assignments.

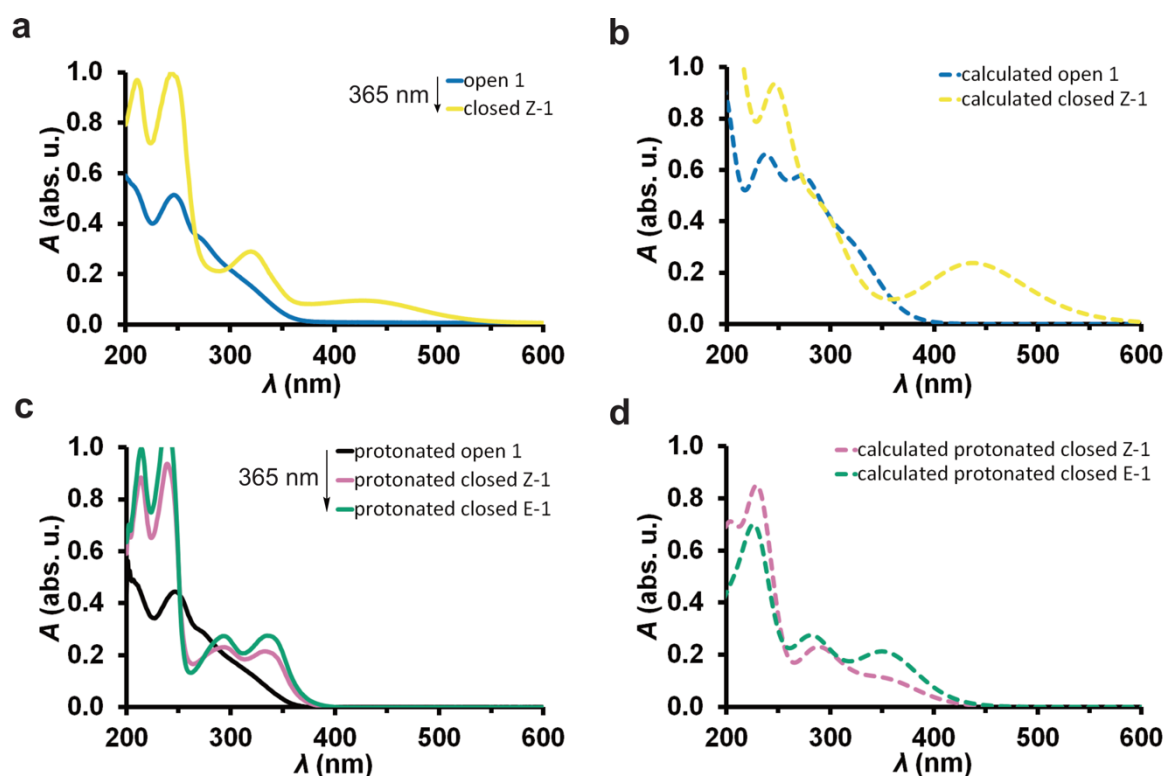


Figure 3 Experimental and calculated (TPSS0-D3BJ/def2-TZVPP-CPCM(Methanol) level of theory) UV/Vis spectra of aza-diarylethene **1**. Experimentally derived spectra were measured in MeOH without or in the presence of 5 equiv. TFA at 23 °C in mM concentrations to be comparable to NMR experiments. **a** UV/Vis absorption of open **1** before (blue) and after irradiation with 365 nm (yellow). **b** Theoretically obtained UV/Vis absorption spectra of open **1** (dotted blue) and closed Z-**1** (dotted yellow) in MeOH. **c** UV/Vis absorption of protonated open **1** before (black) and after irradiation with 365 nm (magenta and green). First protonated closed Z-**1** (magenta) is formed and afterwards protonated closed E-**1** (green). **d** Theoretically obtained UV/Vis absorption spectra of protonated closed Z-**1** (dotted magenta) and protonated closed E-**1** (dotted green) in MeOH.

In conclusion, we report on a unique aza-diarylethene photoswitch motive, which undergoes a highly unusual yet fully reversible zwitterion forming photoreaction. This photoreaction establishes a new C=N bond under concomitant aromatization and thiophene ring opening. The colored and charge-separated photoproduct is metastable and converts back to the open aza-diarylethene form quantitatively in the dark. The kinetics of this thermal reaction can reversibly be adjusted from a dissipative behavior in neutral protic solvents to a highly stable one at low pH. Another *E/Z* isomerization photoreaction can also be established at low pH to turn the aza-diarylethene into a three-state photoswitch. Thus, the first example of photochemical C=N

bond formation and breaking in diarylethenes is delivered, opening up a new class of multi-state photoswitches with unusual solvatochromic, electronic, and pH-responsive behavior. We expect equally exceptional applications for this photoswitch type and direct our future efforts especially at harnessing the exquisite photocontrol over charge separation and corresponding modulation of chemical reactivity.

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Keywords: photoswitch • photochromism • aza-diarylethene • zwitterion • charge-transfer

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