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http://dx.doi.org/10.1002/chem.201904309

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To be cited as: 10.1002/chem.201904309

Link to VoR: https://doi.org/10.1002/chem.201904309

Visible light photoswitching by azobenzazoles

Aaron D. W. Kennedy,[a] Isolde Sandler,[a] Joakim Andréasson,[b] Junming Ho [a] and Jonathon E. Beves*[a]

Abstract: Three visible-light responsive photoswitches are reported, azobis(1-methyl-benzimidazole) (**1**), azobis(benzoxazole) (**2**) and azobis(benzothiazole) (**3**). Photostationary distributions are obtained upon irradiation with visible light comprising ≈ 80% of the thermally unstable isomer, with thermal half-lives up to 8 min and are mostly invariant to solvent. On protonation, compound **1**H$^+$ has absorption extending beyond 600 nm, allowing switching with yellow light, and a thermal half-life just under 5 minutes. The two isomers have significantly different pK_a values, offering potential as a pH switch. The absorption spectra of **2** and **3** are insensitive to acid, although changes in the thermal half-life of **3** indicate more basic intermediates that significantly influence the thermal barrier to isomerization. These findings are supported by high-level ab initio calculations which validate that protonation occurs on the ring nitrogen and that the *Z* isomer is more basic in all cases.

Introduction

Azobenzene is the quintessential example of a photoswitch,[1] undergoing a reversible *E* to *Z* isomerization upon exposure to light irradiation.[1c, 2] Azobenzene, and related derivatives, hold a privileged position amongst photochromic molecules due to the pronounced structural changes associated with the isomerization process, their good conversion from the thermally stable *E* isomer to the unstable *Z* isomer, and their excellent photostability. These molecules have been widely exploited for applications such as molecular machines,[3] information storage,[4] biological conjugates,[5] stimuli-responsive polymers,[6] nanoparticles,[7] and materials.[8]

Related compounds that have one or both of the phenyl rings replaced by a heteroaromatic ring are known as azoheteroarenes.[9] These compounds allow tuning of switching rates, degree of isomerization, and absorption, although they remain much less widely studied than azobenzene derivatives.[10] They are frequently employed in the context of photopharmacology, as many typical pharmacophores contain aromatic heterocycles.[11] Moreover, azoheteroarenes allow for light modulation of molecular properties such as magnetism,[12] luminescence,[13] and pK_a.[14] Arylazopyrazoles,[6e, 15] a class of azoheteroarenes, can undergo light-driven bidirectional switching between the *E* and *Z* isomers and display some of the longest thermal half-lives ($t_{½}$) for the *Z*→*E* isomerization of azo derivative photoswitches ($t_{½}$ = 1000 d).[15a] These half-lives are comparable to the state-of-the-art tetra-*o*-fluoroazobenzenes developed by the Hecht group[16] that also have photostationary distributions (PSDs) highly enriched in the *Z* isomer upon irradiation with visible light (Figure 1).

There are strong motivations for developing visible-light responsive[16-17] azobenzene-type photochromic molecules, including for biological applications.[18] Azo compounds possessing an electron donating and an electron withdrawing group on either side of the azo group ("push-pull" systems) can shift the absorption into the visible.[19] However, these push-pull systems often possess very short (µs to ms) thermal half-lives due to resonance or tautomerization resulting in a weakened azo bond.[1c, 20]

Protonation of azobenzenes can also result in a red-shift of the absorption, such as in the *ortho*-ether azobenzenes developed by the Woolley group.[18c, 21b, 22] Protonated azo-compounds typically have thermal half-lives for the *Z*→*E* isomerization on the order of µs to ms, again due to a decrease in the azo double bond character,[1c, 23] which can limit the accessible population of the *Z* isomer in acidic solutions.[18e, 24]

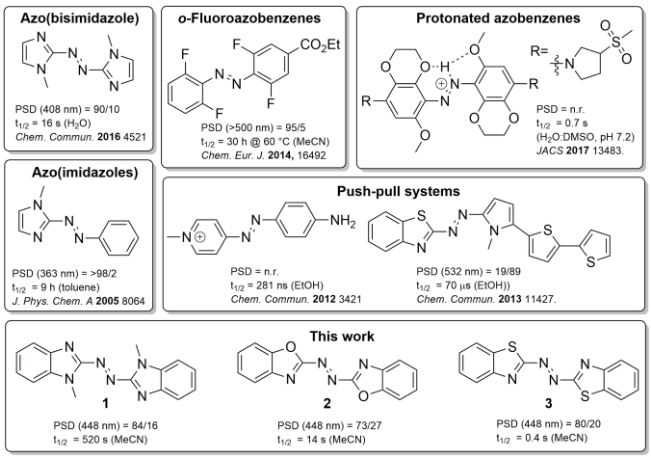

Figure 1. Literature azobenzene-type photochromic molecules[14, 16b, 19a, 19b, 21] and compounds **1–3** prepared in this study. n.r. = not reported. PSD is reported as the *Z*:*E* ratio.

Azobis(2-imidazole)[14, 25] (Figure 1), a symmetric azoheteroarene reported by the Fuchter group, absorbs blue light and is protonated preferentially on the imidazole nitrogen leading to a red-shift in absorption and an *increase* in thermal half-life (from 16 to 352 s in H_2O). An intramolecular hydrogen bond stabilizes the protonated *Z* isomer and leads to a significant difference in proton affinity between the two isomers

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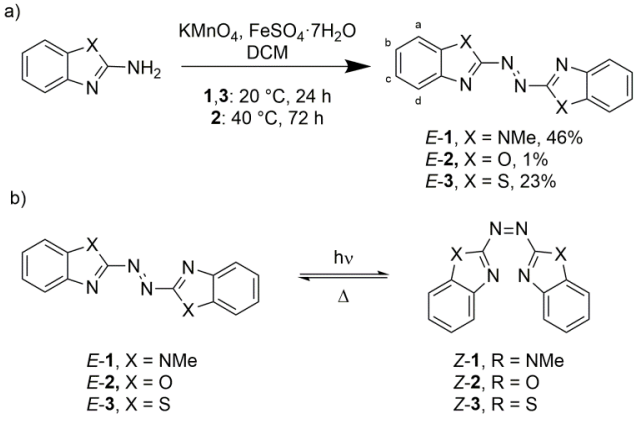
(pK_a values in water: *E* 4.7; *Z* 6.0), which can be used to reversibly modulate the pH of a solution.[14]

An obvious strategy to shift the absorption of an azobenzene-type molecule into the visible is to extend the conjugation of the system. Although the use of symmetric systems prevents the effective use of the symmetry forbidden n–π* transition,[26] it does avoid the potential problems of push-pull systems or relying on protonation to deliver visible light absorption. In this work we report the photoswitching properties of symmetric azobenzazole photoswitches **1**–**3**. These compounds have absorption maxima in the visible spectrum, thermal half-lives up to 8 minutes and are responsive to pH stimuli, including in one case reversible switching with yellow light (λ_{ex} = 591 nm).

Results and Discussion

Symmetric azobenzazoles **1**,[27] **2** and **3**[28] were synthesized in a single step by oxidative coupling of the commercially available amino compounds. The coupling used $KMnO_4$ supported on $FeSO_4{\cdot}7H_2O$[29] giving **1**–**3** in low to moderate yields with a simple work up (Scheme 1). The *N*-methylated benzimidazole was used to form **1** as free amine groups *ortho* to the azo group are known to cause fast thermal relaxation through tautomerism.[14, 21a, 30]

No care was taken to exclude light from the preparation of these compounds, and ^{1}H NMR spectroscopy in $CDCl_3$ indicated the presence of a single symmetric isomer in solution (Figures S2, S10 and S18), assigned to the *E* isomer in all cases. DFT calculations (M06-2X/6-31+G(d,p) and SMD implicit solvent model, see SI-16.1-16.3) indicated that the *E* isomer is at least 42 kJ mol^{-1} lower in energy than the *Z* isomer for each of compounds **1**–**3**, in line with expectations.[31]



Scheme 1 a) Synthesis of symmetric azobenzazoles in this work. b) Photoswitching from the thermally stable *E* isomer to the unstable *Z* isomer.

Compounds **1**–**3** were characterized in detail using 1D and 2D NMR techniques, electrospray ionization mass spectrometry (ESI-MS) and single crystal X-ray diffraction (see SI-3 and SI-4).[32] Single crystals of compounds **1**–**3** were grown by slow solvent evaporation, allowing determination of their solid-state structures (e.g. Figure 2). The crystal structures of **1**–**3** each have half a molecule in the asymmetric unit, with an inversion center in the middle of the azo bond. The rings are therefore coplanar, and the molecules each adopt the *anti*-configuration about the azo bond. The N=N bond lengths are slightly longer than average for azobenzene containing structures ranging from 1.266(2) Å to 1.276(2) Å.[33]

The UV-vis absorption properties of **1**–**3** were characterized in solution (Figure 3). The UV-visible absorption spectra after equilibration in the dark at room temperature were assigned to 100% *E* isomer, consistent with the single species observed by ^{1}H NMR spectroscopy. Compound **1** has a broad absorption band with a maximum at 439 nm (in acetonitrile, assigned as a π–π* transition), red-shifted by ≈ 40 nm relative to that of azobis(2-imidazole), see SI-8. Compounds **2** and **3** also absorb strongly in the visible with slightly narrower π–π* absorption bands at 430 and 421 nm respectively.

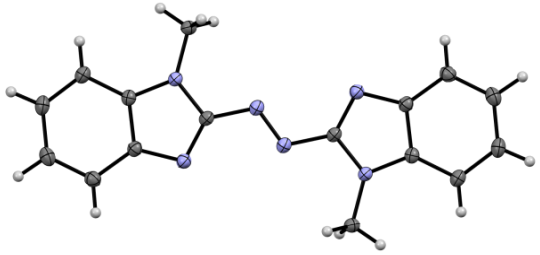


Figure 2. Single crystal X-ray structure of **1**. The asymmetric unit contains half a molecule of **1**. The *N*-Me groups are oriented *anti* with respect to each other. The molecule is engaged in complementary non-classical hydrogen-bonding between the proton of a methyl group and the azo-group of an adjacent molecule (C···N distance = 3.42 Å), not shown.

The absorption spectra of **1**–**3** are relatively insensitive to solvent. The wavelength of maximum visible absorption, λ_{max}, varies by < 10 nm as the solvent is varied (methanol, acetonitrile, dichloromethane, chloroform, or toluene, see SI-5). Acetonitrile solutions of compounds **1**–**3** were irradiated with blue light (448 nm) to enrich the samples in the thermally unstable *Z* isomer, giving a photostationary distribution of isomers (PSD) comprising ≥ 73 % of the *Z* isomer in all cases (Table 1). Figure 4a shows the spectra recorded before and after irradiation at 448 nm.

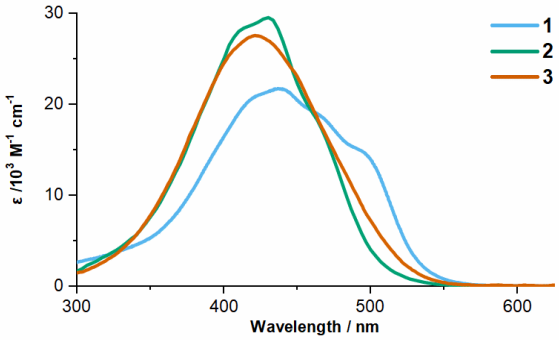


Figure 3. UV-Visible absorption spectra of **1**–**3** in acetonitrile at 298 K (pure *E*-isomer in all cases).

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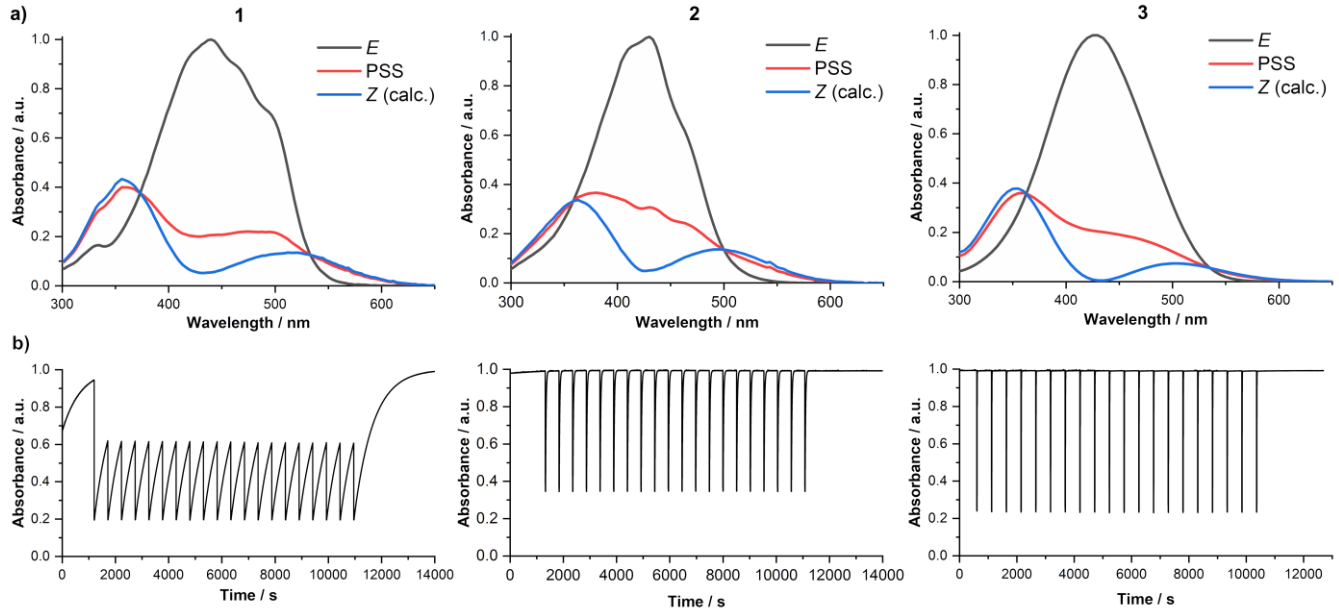

Figure 4 Photoswitching of **1**-**3** in acetonitrile. a) Comparison of the absorption spectra of the pure *E* isomer, the PSS (recorded under 448 nm irradiation) and calculated pure *Z* isomer. The *Z* isomer spectra were calculated using the assumption that the PSS spectrum is a linear combination of *E* and *Z* isomer spectra. b) 20 switching cycles of alternating irradiation (10 seconds, 448 nm LED, 1.3 W) and dark (500 seconds) at 298 K. Absorbance values were measured at the λ_{max} for each compound.

Like their absorption spectra, the PSD of **1**–**3** are largely independent of solvent. Absorption spectra and switching cycles of **1**–**3** in acetonitrile, methanol, chloroform, dichloromethane and toluene are shown in SI-9 to SI-11, with corresponding data in Tables S1, S3 and S4.

The PSD of compound **1** in these solvents comprises between 87–84% of the *Z* isomer as the bands of the two isomers are similarly separated, and the relative quantum yields of switching are comparable, in the solvents studied. Similarly, the PSD for compound **3** is 81–77% of the *Z* isomer in these solvents. Compound **2** has a slightly lower proportion of the *Z* isomer in the PSD (78–73%, except in methanol) due to the stronger relative absorption of the *Z* isomer at 448 nm. In methanol the PSD for **2** comprises only 45% of the *Z* isomer, although some photo decomposition is also observed, hinting at more complicated behavior (Figure S46). Each of **1**–**3** also has excellent fatigue resistance (≥ 99% recovery/cycle) in all solvents tested (Figure 4b).

Examples of a single switching cycle for each of **1**–**3** in acetonitrile are shown in Figure 5 and key parameters are summarized in Table 1. The difference in the thermal half-life ($t_{½}$) for the *Z*→*E* isomerization is immediately apparent. Compound **1** has a half-life of 520 s in acetonitrile, which is among the longest known for visible light switchable azoheteroarenes.[34] Compounds **2** and **3** have shorter half-lives of 14 and 0.4 s respectively, showing that small differences in structure can drastically alter the photoswitching properties.

Calculated geometries (see SI-16.1-16.3 for computational details and Table S23) show for each of **1**–**3** that the *Z* isomer has a twisted (non-planar) conformation in the ground state.

Table 1. Key photoswitching parameters for **1**, **2** and **3** in acetonitrile.[a]

Compound	PSD (*Z*:*E*) [b]	$t_{½}$ / s [c]	Thermal *E* to *Z* barrier / kJ mol^{-1} [d]	% Recovery / cycle [e]
Azobis(2-imidazole)[14]	80:20 [f]	175 [f]	87	—
1	84:16	520	89	> 99.9%
2	73:27	14	80	> 99.9%
3	80:20 [g]	0.4	72	> 99.9%

[a] Measured in dry acetonitrile at 298 K by UV-vis spectroscopy. [b] Upon irradiation with 448 nm light. See SI-7 for discussion on calculation of PSD. [c] Thermal half-life of *Z* to *E* isomerization, see SI-6 for details. [d] Calculated from half-life. [e] Calculated after 20 switching cycles (10 s light irradiation). [f] Data from this work. Solution was irradiated at 448 nm for ease of comparison, however reported maximum switching (90:10) is with 408 nm irradiation.[14] [g] Maximum *E* isomer remaining in the PSD. See SI-7 for details.

Fuchter and co-workers have previously shown that substituents (or atoms with lone pairs) in the *ortho* position to an azo group can lead to such twisted configurations[15d] which do not benefit from stabilizing dispersive interactions in the *Z* isomer. This suggests that the related unsymmetrical compounds where one side of the azo bond is replaced with a phenyl ring could have considerably longer half-lives, although potentially at the expense of the visible-light photoswitching.

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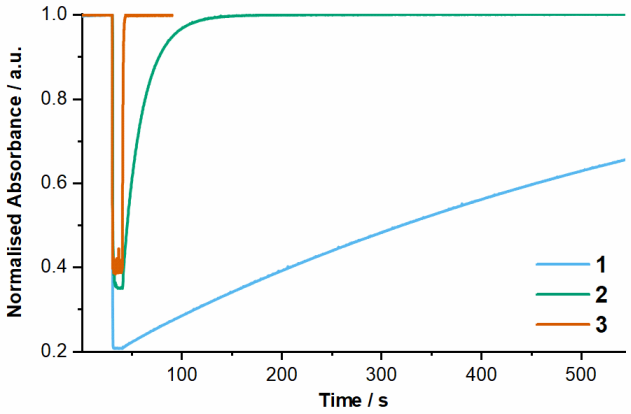

Figure 5 Normalized absorption of **1**, **2** and **3** each measured at λ_{max} in acetonitrile and subjected to irradiation with a 448 nm LED (1.3 W) for 10 s, followed by thermal equilibration in the dark. Further irradiation had no effect on the absorbance value, see Figures S35, S41 and S47

The effect of solvent on the rate of thermal isomerization was also studied for **1**–**3**. The thermal half-life for the *Z*→*E* isomerization of compound **1** ranges from 100 s in toluene to 520 s in acetonitrile, corresponding to a 4 kJ mol^{-1} increase in the thermal barrier. Compound **2** shows much faster thermal isomerization in all solvents ($t_{½} \leq 31$ s). Compound **3** shows the most pronounced solvent sensitivity: the difference between the thermal half-life in acetonitrile (0.4 s) and toluene (84 s) corresponds to an increase in thermal barrier of 13 kJ mol^{-1} (see Table 2). The observed thermal half-lives appear to roughly correlate with solvent polarity, *i.e*. more polar solvents result in shorter thermal half-lives.

Table 2. Comparison of key photoswitching parameters for **3** in a range of solvents [a]

Solvent (E_T^N) [b]	PSD (*Z*:*E*) [c]	$t_{½}$ / s [d]	Apparent thermal barrier / kJ mol^{-1} [e]
Toluene (0.099)	81:19	84	85
Chloroform (0.259)	77:23	32	81
Dichloromethane (0.309)	79:21	39	83
Acetonitrile (0.406)	80:20 [g]	0.4	72
Methanol (0.762)	78:22	1	75

[a] Measured at 298 K by UV-vis spectroscopy. [b] E_T^N = empirical solvent parameter, a measure of solvent polarity.[35] [c] Upon irradiation with 448 nm light. Calculated PSD are for maximum E isomer remaining, based on the assumption that absorbance must always be positive. See SI-7 for discussion on calculation of the PSD. [d] Apparent thermal half-lifetime for the Z→*E* isomerization averaged over 10 cycles of switching (10 s, 448 nm LED irradiation). [e] Calculated from measured $t_{½}$ values.

We wanted to use *in situ* irradiation coupled with ^{1}H NMR spectroscopy[36] to confirm the PSD we calculated from UV-visible absorption data. Due to the relatively short thermal half-lives, intense light and low sample concentrations are required for accurate determination of the PSD at room temperature. These conditions are easily achieved for UV-visible absorption studies but difficult at the concentrations required for ^{1}H NMR experiments. Therefore, ^{1}H NMR experiments were conducted at low temperature (243 K) in $CDCl_3$ to slow the thermal reversion. Light irradiation *in situ* was used to generate the *Z* isomer using the same light source as for UV-visible absorption experiments.[37] The ^{1}H NMR spectra for **3** equilibrated in the dark, and at the PSS, are shown in Figure 6 and SI-12.3, and the related data for **1** and **2** are given in SI-12.1 and 12.2. Only two species were observed, allowing assignment of the ^{1}H NMR signals for the *Z* isomer.

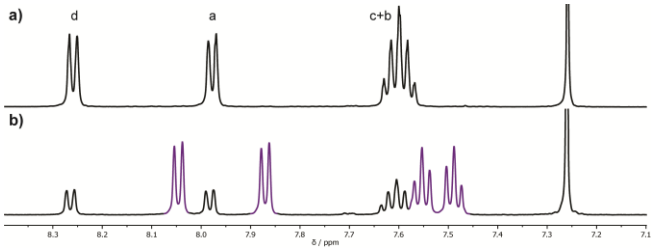

Figure 6. Partial ^{1}H NMR spectra ($CDCl_3$, 500 MHz, 243 K) showing *in situ* photoswitching (448 nm irradiation) of **3**. a) Initial thermally equilibrated spectrum. b) After irradiation with 448 nm light. Black: *E*-**3**, Purple: *Z*-**3**. Labelling is as shown in Scheme 1.

The isomer ratio (75:25) is very close to that found at room temperature by UV-visible absorption data (77:23). This data gives confidence in the PSD we have determined by UV-visible spectroscopy, as the distributions are essentially insensitive to solvent. The calculated *Z*→*E* thermal isomerization barrier was identical to that found from UV-vis spectroscopy at room temperature (80 kJ mol^{-1}, Table S7).

The effects of acid on the properties of the photoswitches were studied by UV-vis and ^{1}H NMR spectroscopies (SI-13 and SI-14). Compounds **2** and **3** only show minor changes in their ^{1}H NMR spectra ($CDCl_3$ or CD_3CN) on the addition of excess trifluoroacetic acid (TFA), (see Figure 7 and Figures S64, S67, S78, S85). However, the ^{1}H NMR signals for **1** are shifted significantly downfield on the addition of acid, consistent with protonation (Figures S61 and S74). Similar effects were observed by UV-vis absorption spectroscopy in acetonitrile.[38] Additions of TFA (up to 15,000 equiv.) to acetonitrile solutions of **2** or **3** did not cause significant changes in their absorption spectra, consistent with the ^{1}H NMR data (Figures S76, S80 and S83). Compound **2** also showed no change in the thermal $t_{½}$ on acid addition (Figure S77). It is clear that compound **2** is not protonated under these conditions.

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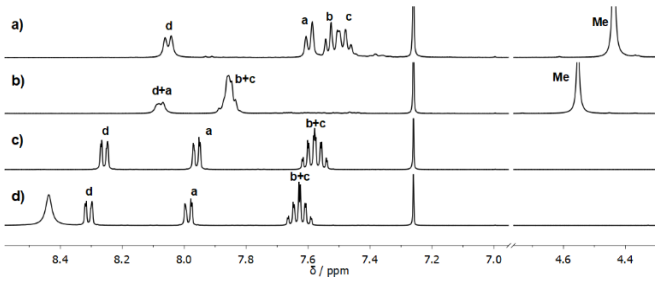

Figure 7. Partial ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) showing the effect of adding TFA to **1** (17 mM) and **3** (23 mM). In both cases [TFA] = 200 mM. a) **1** in $CDCl_3$; b) **1** + TFA in $CDCl_3$; c) **3** in $CDCl_3$ and d) **3** + TFA in $CDCl_3$. At all acid concentrations only one ^{1}H NMR signal is observed for the methyl groups of **1**, indicating acid does not cause any isomerization to the *Z* isomer. Labelling is as shown in Scheme 1.

In dry acetonitrile and in the absence of acid, compound **3** has the shortest half-life we measured (0.4 s, Figure S82 and Table S13). This value was found to increase to 2 seconds in the presence of trace water. On addition of TFA (2.5 equiv.) the half-life *increases* ($t_{½}$ = 43 s), corresponding to a 12 kJ mol^{-1} increase in the thermal *Z*→*E* barrier. Further addition of TFA (up to 250 equiv.) has no effect on the half-life, or on the PSD spectrum. This observed lack of changes suggests that *E*-**3** is not substantially protonated under these conditions. Similarly, the insensitivity to acid of the PSD spectrum suggests that *Z*-**3** is not protonated. We therefore propose at low concentrations of acid there exists some protonated transition state that causes a substantial increase in the thermal isomerization barrier. The identity of this species remains unclear, but potentially could be due to the mechanism of isomerization changing from rotation to inversion, which is generally associated with slower kinetics.[9m] Further TFA additions to the solution decrease the thermal half-life (15,000 equiv. TFA, $t_{½}$ = 6 s, Figure S84 and Table S14). At high acid concentrations a small amount of *Z*-**3**H$^+$ is likely formed, with a significantly shorter half-life than *Z*-**3**, leading to the observed decrease in thermal half-life.

In contrast to the lack of absorption changes for **2** and **3**, an acetonitrile solution of **1** showed a significant red-shift in the absorption ($\Delta\lambda_{max}$ = 62 nm to λ_{max} = 503 nm) and an increase in absorbance upon excess TFA addition (≈ 50 equiv., Figure 8a), consistent with protonation under these conditions. A titration of TFA into an acetonitrile solution of **1** monitored by UV-visible absorption was largely consistent with a single protonation event and suggests a pK_a for *E*-**1**H$^+$ in acetonitrile around 11 (Figure S70; See SI-15 for calculation).

At high acid concentrations (≈ 50 equiv.) both the *Z* and *E* isomers of **1** are protonated (*E*-**1**H$^+$ and *Z*-**1**H$^+$) and these species have overlapping absorption bands. However, the molecule can still be switched upon irradiation with 448 nm light (See Figure S73). The thermal half-life of *Z*-**1**H$^+$ ($t_{½}$ = 280 s, Figure 9, S72 and Table S11) remains relatively long compared to other examples of protonated azobenzenes[23a] (typically μs,[18e] but some examples of minutes have been reported[15e]), or push-pull systems (typically ms to s[1c, 20b]).

The absorption of *E*-**1**H$^+$ extends past 600 nm, allowing switching with visible light, and we demonstrate that we can build up a significant population of the *Z*-**1**H$^+$ isomer by irradiation at 591 nm in acetonitrile (SI-14.2). The absolute change in absorbance is limited (14%) however it has been suggested for related compounds[14] that both protonated isomers have similar absorption spectra. Therefore, the *Z*:*E* ratio in the PSD could not be accurately determined.

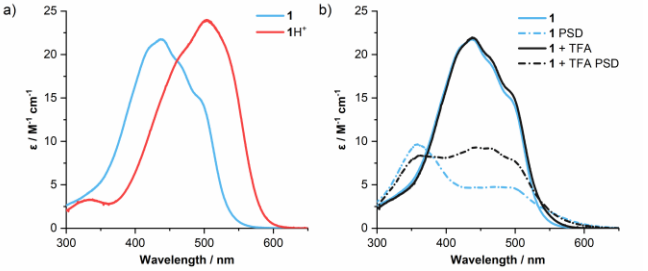

Figure 8. The response of **1** (50 μM in CH_3CN) to TFA addition. a) Comparison of UV-vis absorption of **1** and **1**H$^+$ in CH_3CN. **1**H$^+$ was generated by the addition of ≈ 50 equivalents of TFA (final [TFA] = 2.5 mM) into a solution of **1** in CH_3CN. b) The effect of adding 2.5 equiv. of TFA to **1** in CH_3CN. **1** + TFA refers to a solution of **1** in CH_3CN upon addition of 2.5 equivalents of TFA (final [TFA] = 125 μM). PSS were generated by irradiation with a 448 nm LED.

To improve our understanding of these phenomena, we used DFT, DLPNO-CCSD(T)/CBS[39] and the SMD implicit solvent model[40] calculations to determine the optimized geometries and energies of the isomers of **1**–**3**, and their various protonated forms. The lowest energy conformations were calculated for the protonated molecules where either the ring or azo nitrogen is protonated for both the *E* and *Z* isomers (see SI-16.1–16.3). In all cases the protonated azo species were significantly higher in energy (≥ 34 kJ·mol^{-1}) than the alternative species protonated on the ring nitrogen (see Tables S15-17, and Table S18 for calculated pK_a values). Therefore, protonation preferentially occurs on the ring nitrogen.

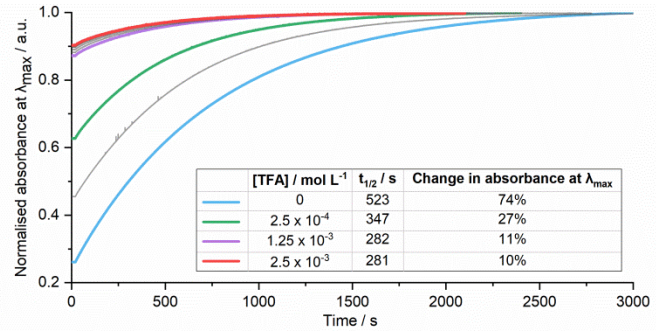

Figure 9. Change in the *Z*→*E* thermal half-life for **1** (acetonitrile, 50 μM, 298 K) as TFA is added. Data were collected in increments of 1.25 x 10^{-4} M in the range from 0 to 2.5 x 10^{-4} M and increments of 2.5 x 10^{-4} M from 2.5 x 10^{-4} to 2.5 x 10^{-3} M. Selected data have been shown in the inset table. Solutions were irradiated with 448 nm light to reach the PSD and then monitored in the dark at the λ_{max} of the absorption band. Calculation of thermal half-life ($t_{½}$) is discussed in SI-6. Colors match the scheme used in Figure 8.

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Protonated compounds *E*-**2**H$^+$ and *E*-**3**H$^+$ are sufficiently acidic in all conformations (calculated pK_a values in acetonitrile ≤ 2) that they should not be protonated at the TFA concentrations we have used, reflected in the lack of changes in the UV-vis and ^{1}H NMR spectra. However, compound *E*-**1**H$^+$ has a calculated pK_a in acetonitrile of 11.7, in good agreement with the measured value (11) and consistent with the observed spectral changes upon addition of TFA.

In all cases, the *Z* isomers of **1**–**3** are calculated to be more basic than the thermally stable *E* isomers (calculated pK_a difference of 1.1 to 2.4 units) due to the formation of an intramolecular hydrogen bond (Figure 10), as observed for related systems.[14, 41] The validity of this interaction was confirmed by atoms-in-molecule analysis, see SI-17. The calculated pK_a values for *Z*-**2**H$^+$ and *Z*-**3**H$^+$ are sufficiently low that these species are not observed upon addition of TFA. However, compound *Z*-**1**H$^+$ has a calculated pK_a in acetonitrile of 12.8 which indicates that at low TFA concentrations *Z*-**1**H$^+$ will be formed preferentially over *E*-**1**H$^+$, explaining the observed sensitivity of the PSD to low concentrations of acid.

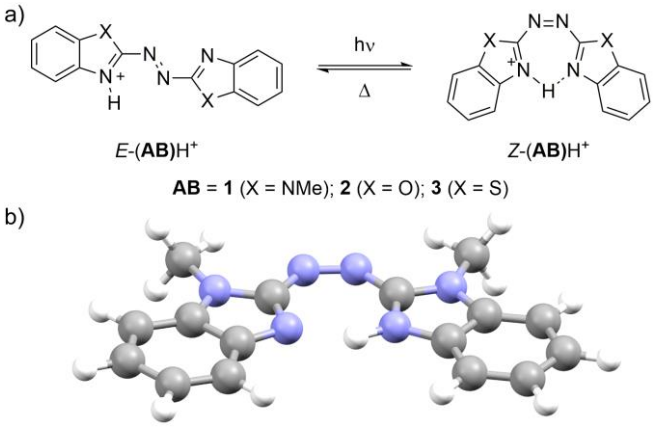

Figure 10. a) Photoswitching of **1**-**3**H$^+$ showing the proposed intramolecular hydrogen bond in the *Z* isomer. b) Optimized geometry for *Z*-**1**H$^+$ in acetonitrile (M06-2X/6-31+G(d,p)) showing the proposed hydrogen bonding interaction and the resulting planarity of the molecule.

Conclusions

We introduce azobenzazoles as visible-light responsive photoswitches, with sufficiently long thermal half-lives (0.4 to 520 s) for many applications. Their absorption properties, thermal half-lives and fatigue resistance were thoroughly characterized in a range of organic solvents. Compound **1** can be readily protonated with TFA and the *Z* isomer is more basic than the *E* isomer due to an intramolecular hydrogen-bond. *E*-**1**H$^+$ has absorption extending past 600 nm and can be photoswitched with 591 nm light. Conversely, compound **2** is unaffected by acid concentration. Compound **3** shows no change in absorption upon acid addition, and yet significant changes in the rates of thermal equilibration consistent with a protonated intermediate that significantly increases the thermal half-life. This later discovery could offer a new mechanism for altering the thermal stability of azobenzene-type photoswitches. Overall, the reported compounds demonstrate photoswitching that can be extended well into the visible, modulated with acid and amongst the longest thermal half-lives of azoheteroarenes switchable with visible light.

Experimental Section

See SI for details of synthesis, characterization data, X-ray crystallography data, UV-vis spectroscopy and photoswitching, computed properties and optimized geometries.

Acknowledgements

The authors acknowledge the Australian Research Council for a Future Fellowship (FT170100094 to JEB), and a DECRA Fellowship (DE160100807 to JH). ADWK acknowledges the Australian Government for an Australian Postgraduate Award and IS acknowledges the support of an Australian Government Research Training Program Scholarship. JA thanks UNSW Science Faculty for a Visiting Research Fellowship. This research was partly undertaken on the MX1 beamline at the Australian Synchrotron, part of ANSTO. Access to the Australian Synchrotron was possible by a Collaborative Access Program (MXCAP12368/13234). Shyamal K. K. Prasad is thanked for help in measuring the LED emission spectra. JH thanks the Australian National Computational Infrastructure (NCI) and UNSW for generous allocation of computing resources.

Keywords: photoswitch • visible-light • photochrome • azobenzene • pH switch

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[34] There are relatively few visible-light responsive azoheteroarenes. The longest half-lives reported to date are for 6-azopurine (530 nm, $t_{½}$ = 46 min, DMSO, Ref 9f); 5-phenylazopyrimidine (405 nm, $t_{½}$ = 8 min, MeCN, Ref. 35d; phenylazoindole (400 nm, $t_{½}$ = 2.6 days, dry DMSO, Ref. 9l; azobis(2-imidazole) (415 nm, $t_{½}$ = 16 s, H_2O, Ref. 14; 448 nm, $t_{½}$ = 3 min, MeCN - this work).

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[38] More complex behavior was observed in chloroform. The observed changes (see Figures S53 and S56) appear to be consistent with partial protonation and a degree of decomposition. However, anion binding effects may be important as some changes were observed in the UV-vis spectra upon addition of chloride anions (Figures S68 and S69).

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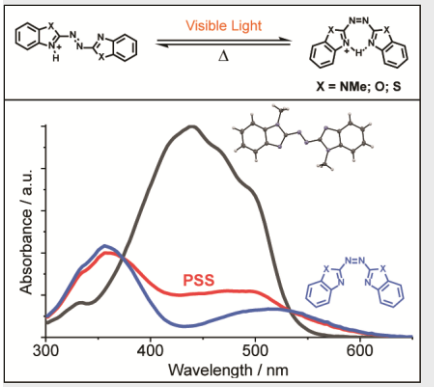
Entry for the Table of Contents

FULL PAPER

Switching it up: Three symmetric azoheteroarenes undergo *E*-to-*Z* isomerization in response to visible light, with excellent fatigue resistance and second to minute thermal half-lives. Acid addition led to a compound that can be isomerized with ≈ 600 nm light.



*Aaron D. W. Kennedy, Isolde Sandler, Joakim Andréasson, Junming Ho and Jonathon E. Beves**

Page No. – Page No.

Visible light photoswitching by azobenzazoles

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