SUPPLEMENTARY INFORMATION

Arylazoindazole Photoswitches: Facile Synthesis and Functionalization via $S_{\text{NAr}}$ Substitution

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Contents

Experimental section ................................................................................................................................. 2
X-ray crystal structure determinations ..................................................................................................... 5
NMR spectral data ..................................................................................................................................... 7
UV/vis spectra for $E$-isomers and photostationary states ...................................................................... 23
UV/vis spectra for $Z$-isomers of 2 and 3 ............................................................................................ 27
Photosiomerization quantum yields ....................................................................................................... 28
Thermal isomerization kinetics ............................................................................................................... 34
Computational studies ............................................................................................................................ 39
Presence of multiple rotamers: influence on quantum yields............................................................... 48
References............................................................................................................................................... 49
Experimental section

**General methods.** The syntheses involving air-sensitive chemicals (KH, Me₂Zn) were carried out under nitrogen atmosphere using standard glovebox, Schlenk, and vacuum-line techniques. Toluene (Aldrich, anhydrous, 99.8%) was passed over columns of Al₂O₃ (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). THF (Aldrich, anhydrous, 99.8%) was dried by percolation over columns of Al₂O₃ (Fluka). These solvents were degassed prior to use and stored under nitrogen. C₆D₆ (Aldrich) was vacuum transferred from Na/K alloy and stored under nitrogen. DMSO-d₆ (Aldrich) and THF-d₈ (Euriso-top) were used without further purification. Solvents for UV-Vis spectroscopy were used as received. Potassium hydride (Sigma-Aldrich, 30 wt % in mineral oil) was washed with hexane several times to remove the oil, and then dried in vacuo to give a powder, which was stored in the glovebox. Dimethylzinc (Acros, 1.2 M solution in toluene) was used as received. The compound PhNNC(C₆F₅)NNHMes was synthesized according to the published procedure. Routine NMR spectra were recorded on Varian Gemini 400 or Varian Inova 500 spectrometers. ¹⁹F, ¹⁹F-COSY and ¹⁹F, ¹⁹F-NOESY NMR spectra were recorded on Agilent 400MR or Varian Inova 500 spectrometers. For the ¹⁹F, ¹⁹F-NOESY experiments, long mixing times (2 s) were used to avoid spurious correlations due to zero-quantum artifacts. ¹H, ¹⁹F-HOESY NMR spectra were recorded on an Agilent 400MR spectrometer (with OneNMR probe) or a Varian 400 MHz VNMRS system (with an Auto Switchable (ASW) probe, with tuning optimized for both ¹H and ¹⁹F). The standard ¹H, ¹⁹F-HOESY experiment present in the VNMRJ software was applied, using ¹⁹F detection. The ¹H and ¹³C NMR spectra were referenced internally using the residual solvent resonances and reported in ppm relative to TMS (0 ppm); J is reported in Hz. Photostationary states were determined by using NMR spectroscopy (Varian Inova 500). Samples were irradiated inside the NMR spectrometer using an optical fiber cable inside of the NMR tube which was connected to 365 nm and 420 nm LEDs for photo-conversion from $E \rightarrow Z$ and $Z \rightarrow E$, respectively. Elemental analyses were performed at the Microanalytical Department of the University of Groningen. UV-vis absorption spectra were measured on an Analytik Jena Specord S600 diode array or a Hewlett-Packard 8453 spectrometer in a 1 cm quartz cuvette. Kinetics of thermal $Z \rightarrow E$ isomerization are measured and analyzed as described in more detail below (section ‘thermal isomerization kinetics’).

**Synthesis of 3-(mesityldiazenyl)-1-phenyl-1H- tetrafluoroinazole (2).** Treatment of formazan 1 (157.9 mg, 0.37 mmol) with 1.5 equiv. of potassium hydride (22.0 mg, 0.55 mmol) as a strong base in THF at room temperature resulted the color to fade from dark to light orange. After stirring at room temperature for 4 h, the solvent was removed in vacuo and a new portion of THF was added. The solution was filtered through a 0.2 micron syringe filter. Subsequent removal of all volatiles gave 142.1 mg of an orange solid which was shown by NMR analysis to be a 1.45:1 mixture of compounds 2 and 3 (0.34 mmol, 94% yield). Anal. calcd. for C₂₂H₁₆F₄N₄: C 64.08, H 3.91, N 13.59; found: C 64.42, H 4.11, N 13.32.

A single recrystallization of the mixture of 2 and 3 from toluene by cooling to -70 °C afforded pure compound 2 (51% isolated yield based on starting material 1). ¹H NMR (C₆D₆, 25 °C, 500 MHz): δ 7.41 (m, 2H, Ph o-H), 7.10 (t, 2H, $J = 7.4$, Ph m-H), 7.03 (1H, $J = 7.4$, Ph p-H), 6.80 (s, 2H, Mes m-H), 2.72 (s, 6H, Mes o-CH₃), 2.09 (s, 3H, Mes p-CH₃). ¹⁹F NMR (C₆D₆, 25 °C, 470 MHz): δ −133.3 (td, 1F, $J = 20.8$, C₆F₄).
overnight, the volatiles were removed on the rotava p and the resulting solid extracted into Et
previously dissolved in 0.5 mL of MeOH. This result ed in an orange suspension, to which more THF was
added until a homogeneous solution was obtained (ca. 4 mL). After stirring at room temperature
NMR (CDCl₃, 0.28 mmol). The mixture was heated to 80
(0.0502 mmol, 80%) of
H Synthesis of 3-(mesityldiazenyl)-1-phenyl-1
137.38 (d, J = 247.0 Hz, C
140.54 (d, J = 252.3 Hz, C₆F₄), 140.12 (d, J = 252.3 Hz, C₆F₄), 140.00 (d, J = 274.0 Hz, C₆F₄), 137.38 (d, J = 247.0 Hz, C₆F₄), 136.31 (Mes o-C), 135.48 (Mes ipso-C), 132.82 (d, J = 252.3 Hz, C₆F₄), 132.18 (Ph p-CH), 129.54 (Ph m-CH), 129.37 (Mes m-CH), 128.54 (d, C₆), 123.60 (Ph o-CH), 103.28 (C₆), 21.09 (Mes p-CH₃), 17.30 (Mes o-CH₃).

* long-range C-F coupling within the C₆F₄ ring (ca. 8 – 20 Hz) and smaller C-F coupling (< 5 Hz) in some of the Mes and Ph resonances is observed but not reported.

Synthesis of 3-(phenyldiazenyl)-1-mesityl-1
Ph
ipso
H Synthesis of 3-(phenyldiazenyl)-1-mesityl-1
128.54 (d, C₆), 129.09 (Ph p-CH), 126.61 (d, C₆), 125.09 (d, J CF = 2.9, Ph o-CH), 104.89 (C₆), 21.19 (Mes p-CH₃), 20.66 (Mes o-CH₃).

* long-range C-F coupling within the C₆F₄ ring (ca. 8 – 20 Hz) and smaller C-F coupling (< 5 Hz) in some of the Mes and Ph resonances is observed but not reported.

Synthesis of 3-(mesityldiazenyl)-1-phenyl-1H-4,5,7-trifluoro-6-methoxyindazole (4). To a solution of 25.8 mg of 2 (0.0626 mmol) in 0.5 mL of THF was added 12.5 mg NaOH (0.313 mmol, 5 equiv), which was previously dissolved in 0.5 mL of MeOH. This resulted in an orange suspension, to which more THF was added until a homogeneous solution was obtained (ca. 4 mL). After stirring at room temperature overnight, the volatiles were removed on the rotavap and the resulting solid extracted into Et₂O (2 x 3 mL). Attempts to recrystallize the product were unsuccessful; a light orange powder was invariably obtained. The product was finally isolated by cooling a hot MeOH solution to -30 °C, which gave 21.3 mg (0.0502 mmol, 80%) of 4. HRMS (ESI) calcd. for C₂₃H₂₀F₃N₄O [M+H⁺] 425.15837, found 425.15849. ¹H NMR (CDCl₃, 25 °C, 500 MHz): δ 7.67 (d, J = 7.3, 2H, Ph o-H), 7.54 (t, J = 7.3, 2H, Ph m-H), 7.48 (d, J = 7.3,
1H, Ph p-H), 6.98 (s, 2H, Mes m-H), 4.11 (s, 3H, OMe), 2.53 (s, 6H, Mes o-Me), 2.35 (s, 3H, Mes p-Me). \(^{19}\)F NMR (CDCl\(_3\), 25 °C, 470 MHz): δ -134.3 (t, J = 20, 1F, 4-F), -147.7 (d, J = 19.3, 1F, 7-F), -156.0 (d, J = 21.2, 1F, 5-F).

\(^{13}\)C NMR* (CDCl\(_3\), 25 °C, 100 MHz): δ 156.9 (NNCNN), 148.9 (Mes ipso-C), 140.9 (d, J = 246, C\(_6\)F\(_3\)), 140.2 (Mes p-C), 139.5 (d, J= 256, C\(_6\)F\(_3\)), 139.5 (Ph ipso-C), 137.8 (C-OMe), 136.6 (d, J = 248, C\(_6\)F\(_3\)), 133.4 (Mes o-C), 130.4 (Mes CH), 129.0 (Ph m-CH), 128.8 (Ph p-CH), 127.6 (C\(_A\)), 125.5 (Ph o-CH), 103.7 (C\(_B\)), 62.6 (OMe), 21.4 (Mes p-Me), 20.1 (Mes o-Me).

* long-range C-F coupling within the C\(_6\)F\(_4\) ring (ca. 8 – 20 Hz) and smaller C-F coupling (< 5 Hz) in some of the Mes and Ph resonances is observed but not reported.

** this signal is of low intensity and overlaps with an impurity, and as a consequence its assignment is somewhat ambiguous.

** Synthesis of 3-(mesityldiazenyl)-1-phenyl-1H-4,5,7-trifluoro-6-(octylthio)indazole (5). To a solution of 16.2 mg of 2 (0.0393 mmol) in 0.4 mL of THF-d\(_8\) was added 7.2 mg C\(_8\)H\(_{17}\)SK (0.0393 mmol), which was previously suspended in 0.2 mL of THF-d\(_8\). This resulted in an orange solution (with some white precipitate, presumably KF). The mixture was analyzed after 30 minutes by \(^1\)H and \(^{19}\)F NMR, which showed > 90% conversion of the starting materials and formation of the desired compound 5. After standing at room temperature overnight, the volatiles were removed on the rotavap and the resulting solid extracted into Et\(_2\)O (2 x 3 mL). Removal of the volatiles gave 21.1 mg (0.0392 mmol, 99%) of 5 as a somewhat sticky orange powder that was > 90% pure based on NMR spectroscopy. HRMS (ESI) calcd. for C\(_{30}\)H\(_{34}\)F\(_3\)N\(_4\)S [M+H\(^+\)] 539.24508, found 539.24374.

\(^1\)H NMR (CDCl\(_3\), 25 °C, 500 MHz): δ 7.66 (br d, J = 7.2, 2H, Ph o-H), 7.55 (t, J = 7.3, 2H, Ph m-H), 7.49 (t, J = 7.3, 1H, Ph p-H), 6.98 (s, 2H, Mes m-H), 2.95 (t, J = 7.2, 2H, SCH\(_2\)), 2.35 (s, 6H, Mes o-Me), 2.25 (s, 3H, Mes p-Me), 1.65-0.8 (C\(_8\)H\(_{17}\)).

\(^{19}\)F NMR (CDCl\(_3\), 25 °C, 470 MHz): δ -120.1 (d, J = 21.4, 1F, 7-F), -135.1 (t, J = 22.1, 1F, 4-F), -136.1 (d, J = 22.8, 1F, 5-F).

\(^{13}\)C NMR* (CDCl\(_3\), 25 °C, 100 MHz): δ 156.8 (NNCNN), 148.9 (Mes ipso-C), 145.6 (d, J = 241, C\(_6\)F\(_3\)), 143.2 (d, J = 247, C\(_6\)F\(_3\)), 140.3 (Mes p-C), 139.5 (Ph ipso-C), 139.1 (d, J = 255, C\(_6\)F\(_3\)), 133.5 (Mes o-C), 130.4 (Mes CH), 129.1 (Ph m-CH), 128.9 (Ph p-CH), 127.9 (C\(_A\)), 125.7 (Ph o-CH), 113.5 (C-SOct), 108.9 (C\(_A\)), 35.1 (SCH\(_2\)), 31.9 (octyl), 30.3 (octyl), 29.2 (octyl), 29.1 (octyl), 28.6 (octyl), 22.8 (octyl), 21.4 (Mes p-Me), 20.2 (Mes o-Me), 14.2 (octyl-Me).

* long-range C-F coupling within the C\(_6\)F\(_4\) ring (ca. 8 – 20 Hz) and smaller C-F coupling (< 5 Hz) in some of the Mes and Ph resonances is observed but not reported.
X-ray crystal structure determinations

Single crystals of compound $E$-2 and $E$-3 were mounted on top of a cryoloop and transferred into the cold nitrogen stream (100 K) of a Bruker-AXS D8 Venture diffractometer. Data collection and reduction was done using the Bruker software suite APEX2. The final unit cell was obtained from the xyz centroids of 9942 ($E$-2) and 9977 ($E$-3) reflections after integration. A multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS). The structures were solved by direct methods using SHELXS ($E$-2) or SHELXT ($E$-3) and refinement of the structure was performed using SHELXL. The hydrogen atoms were generated by geometrical considerations, constrained to idealised geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Crystal data and details on data collection and refinement are presented in Table S1.

**Table S1.** Crystallographic data for $E$-2 and $E$-3

|         | $E$-2                                | $E$-3                                |
|---------|--------------------------------------|--------------------------------------|
| chem formula | $C_{22}H_{16}F_{4}N_{4}$             | $C_{22}H_{16}F_{4}N_{4}(C_{6}H_{6})_{0.5}$ |
| $M_r$   | 412.39                               | 451.44                               |
| cryst syst | orthorhombic                        | monoclinic                          |
| color, habit | orange, needle                      | orange, needle                      |
| size (mm) | 0.28 x 0.08 x 0.03                   | 0.12 x 0.07 x 0.03                   |
| space group | Pbcn                                | P2$_1$/c                             |
| a (Å)   | 13.194(3)                            | 6.7441(4)                            |
| b (Å)   | 38.114(7)                            | 23.0301(13)                          |
| c (Å)   | 14.650(3)                            | 14.3273(9)                           |
| $\beta$ (deg) |                                  | 103.073(2)                           |
| $V$ (Å$^3$) | 7367(3)                              | 2167.6(2)                            |
| $Z$     | 16                                   | 4                                    |
| $\rho_{\text{calc}}, \text{g.cm}^{-3}$ | 1.487                                 | 1.383                                |
| $\mu(\text{Mo K}\alpha), \text{cm}^{-1}$ | 0.119                                 | 0.912                                |
| $\mu(\text{Cu K}\alpha), \text{cm}^{-1}$ |                                  |                                       |
| F(000)  | 3392                                 | 932                                  |
| temp (K) | 100(2)                               | 100(2)                               |
| $\theta$ range (deg) | 2.78 – 26.37                         | 6.343 – 74.722                      |
| data collected (h,k,l) | -16:16, -42:47, -18:18             | -8:8, -28:28, -17:17                |
| no. of rflns collected | 123195                               | 24720                               |
| no. of indpndt reflns | 7546                                 | 4404                                |
| observed reflns | 5109 ($F_o \geq 2 \sigma(F_o)$) | 3725 ($F_o \geq 2 \sigma(F_o)$) |
| R(F) (%) | 5.39                                  | 4.63                                 |
| Parameter                           | Value 1 | Value 2 |
|------------------------------------|---------|---------|
| wR(F²) (%)                         | 12.74   | 10.59   |
| GooF                               | 1.093   | 1.076   |
| Weighting a,b                      | 0.0423, 7.2002 | 0.0353, 1.1040 |
| params refined                     | 547     | 301     |
| restraints                         | 0       | 0       |
| min, max resid dens                | -0.281, 0.281 | -0.196, 0.246 |
Figure S1a. E-2. top: $^1$H-NMR (C$_6$D$_6$, 500 MHz); bottom: $^{19}$F-NMR (C$_6$D$_6$, 470 MHz)
Figure S1b. E-2. top: $^{13}$C-NMR (C$_6$D$_6$, 500 MHz); bottom: $^1$H, $^{19}$F-HOESY (THF-$d_8$)
Figure S1c. *E*-2. top: gHSQC (C$_6$D$_6$, 500 MHz); bottom: gHMBC (C$_6$D$_6$, 500 MHz)
Figure S2. 2-PSS after irradiation at 365 nm. $^1$H-NMR (top) and $^{19}$F-NMR (bottom) in C$_6$D$_{6}$, PSS = 80%. 

80% 2 cis

20% 2 trans

80% 2 cis

20% 2 trans
Figure S3a. E-3. top: $^1$H-NMR (C$_6$D$_6$, 400 MHz); bottom: $^{19}$F-NMR (C$_6$D$_6$, 376 MHz)
Figure S3b. E-3. top: $^{13}$C-NMR (C$_6$D$_6$, 125 MHz); bottom: $^1$H, $^{19}$F-HOESY (C$_6$D$_6$)
Figure S3c. E-3. top: gHSQC (C₆D₆, 500 MHz); bottom: gHMBC (C₆D₆, 500 MHz)
**Figure S4. 3-PSS** after irradiation at 365 nm, $^{19}$F-NMR in C$_6$D$_6$: PSS = 92% (ca. 10% impurities due to presence of Z/E-2)
Figure S5a. E-4. top: $^1$H-NMR (CDCl$_3$, 500 MHz); bottom: $^{19}$F-NMR (CDCl$_3$, 470 MHz)
Figure S5b. E-4. top: $^{13}$C-NMR (CDCl$_3$, 100 MHz); bottom: $^1$H,$^{19}$F-HOESY (CDCl$_3$)
Figure S5c. **E-4.** top: $^{19}$F, $^{19}$F-COSY (CDCl$_3$, 470 MHz); bottom: $^{19}$F, $^{19}$F-NOESY (CDCl$_3$, 470 MHz, mixing time = 2 s)
Figure S6. top: 4-PSS after irradiation at 365 nm, $^{19}$F-NMR in C$_6$D$_6$, PSS = 75%; bottom: 4-PSS after irradiation at 420 nm, $^{19}$F-NMR in C$_6$D$_6$, PSS = 46%;
Figure S7a. E-5. top: $^1$H-NMR (CDCl$_3$, 500 MHz); bottom: $^{19}$F-NMR (CDCl$_3$, 376 MHz; peaks labeled with an asterisk are likely due to double thiolate substitution)
Figure S7b. E-5. top: $^{13}$C NMR (CDCl₃, 100.5 MHz); bottom: $^{19}$F, $^{19}$F NOESY NMR (CDCl₃, 470 MHz)
Figure S7c. E-5. top: HSQC NMR spectrum (THF-d$_8$); bottom: HMBC NMR spectrum (THF-d$_8$)
Figure S8. UPLC-MS of reaction mixture resulting from 1 + KH (4 compounds; 2 and 3 as a mixture of Z/E isomers).
UV/vis spectra for $E$-isomers and photostationary states

**Figure S9.** UV-Vis spectra of 2-E (red) and photostationary state (blue) after irradiation at 365 nm in DMSO.

**Figure S10.** UV-Vis spectra of 2-E (red) and photostationary state (blue) after irradiation at 365 nm in toluene.
**Figure S11.** UV-Vis spectra of 3-E (red) and photostationary state (blue) after irradiation at 365 nm in DMSO.

**Figure S12.** UV-Vis spectra of 3-E (red) and photostationary state (blue) after irradiation at 365 nm in toluene.
Figure S13. UV-Vis spectra of 4-E (red) and photostationary state (blue) after irradiation at 365 nm in DMSO.

Figure S14. UV-Vis spectra of 4-E (red) and photostationary state (blue) after irradiation at 365 nm in toluene.
**Figure S15.** UV-Vis spectra of 5-E (red) and photostationary state (blue) after irradiation at 355 nm in DMSO.

**Figure S16.** UV-Vis spectra of 5-E (red) and photostationary state (blue) after irradiation at 355 nm in toluene.
UV/vis spectra for Z-isomers of 2 and 3

The spectra of the Z-isomers were estimated by taking the spectrum of the photostationary state and subtracting the fraction (determined using NMR spectroscopy) of E-isomer present in the PSS mixture. NMR solutions (\(\sim 10^{-2}\) M in toluene) were irradiated in a quartz cuvette using a 355 nm laser during several hours to ensure the PSS was reached. To check this, a portion of the NMR solution was diluted to \(\sim 10^{-5}\) M and its UV-Vis spectrum was measured. Subsequently, the UV-Vis solution was irradiated at 355 nm, upon which no further changes were observed in the UV-Vis spectrum, indicating that the PSS had been reached. The NMR solution was then transferred to a 5 mm glass NMR tube and the product ratio was determined by integration of the \(^{19}\)F NMR spectrum: PSS\(_{355}\) ratio for 2, E:Z = 32:68; PSS\(_{355}\) ratio for 3, E:Z = 14:86.

Figure S17. UV/vis absorption spectra of E- and (calculated) Z-isomers of compounds 2 (top) and 3 (bottom).
Photosomerization quantum yields

Actinometry

The absolute quantum yield was determined with reference to the actinometer potassium ferrioxalate. Laser flux was determined by the method of total absorption using 2 mL of 6 mM (for 355 nm) and 0.15 M (for 457 nm) potassium ferrioxalate in a 1 cm path length cuvette with stirring. The actinometer was irradiated for 90 s (at 355 nm) and 45 s (at 457 nm), respectively. A reference cuvette was held apart from the excitation source. After irradiation, 1 mL of each solution was added to buffered aqueous phenanthroline (0.1 M, 2 mL), and diluted 10 fold with water and left to stand in the dark for at least 30 min and the absorbance determined at 510 nm. The photon flux was calculated using equation (E1):

\[
(Nh/vt) = \frac{\Delta A}{L \varepsilon \Phi \times t \times F} \times 20
\]  

(E1)

Where L is the path length of the cuvette, \(\varepsilon\) is the molar absorptivity of iron(II) tris-phenanthroline (11100 L mol\(^{-1}\) cm\(^{-1}\) at \(\lambda_{\text{max}}\) 510 nm), \(\Phi\) is quantum yield of the actinometer at 355 nm and 457 nm, \(t\) is the irradiation time, \(F\) is the fraction of the light the actinometer absorbed.

Equations used for quantum yield calculations

The aryloindazole trans-to-cis isomerization was calculated as previously reported.\(^7\)

\[
-V \frac{dC_1}{dt} = \phi_1 \frac{\varepsilon_1 C_1}{D} I (1 - 10^{-D}) - \phi_2 \frac{\varepsilon_2 C_2}{D} I (1 - 10^{-D})
\]

(E2)

\(-V \frac{dC_1}{dt}\) is the change of species A in mole; \(I (1 - 10^{-D})\) is the light absorbed by the whole system; \(\varepsilon_1 C_1 / D\) is the fraction of light absorbed by A; \(C_1, C_2\) are the concentrations of trans and cis isomers (M); \(\varepsilon_1, \varepsilon_2\) are the absorption coefficients of trans and cis isomers at \(\lambda_{\text{irr}}\); \(D\) is the absorbance when using a 1 cm path length cuvette; \(\phi_1, \phi_2\) are the quantum yields for reactions trans to cis, and cis to trans; \(I\) is the photon flux determined by actinometry.

Using mole fractions \(X = \frac{C}{C_0}\), \(C_0 = C_1 + C_2\) is the total concentration, defining \(K = \varepsilon_1 \phi_1 + \varepsilon_2 \phi_2\),

\[
\frac{dX_1}{dt} \cdot \frac{D}{1 - 10^{-D}} = \frac{I}{V} \left( KX_1 - \frac{\varepsilon_2 C_2}{C_0} \right)
\]

(E3)

Using \(R = \frac{\varepsilon_2 C_2}{C_0}\),

\[
\frac{dX_1}{dt} \cdot \frac{D}{1 - 10^{-D}} = \frac{I}{V} (KX_1 - R)
\]

(E4)
Using \( f = \int_0^t \frac{1 - 10^{-D}}{D} \, dt \) and integrating the equation, then

\[
\ln \left( \frac{KX_1 - R}{KX_0 - R} \right) = f \frac{KI}{V}
\]  

(E5)

When the photostationary state is reached, \( \frac{dX_1}{dt} = 0 \),

\[
\left( KX_1 - \frac{\epsilon_2 C_2}{C_0} \right) = 0, \quad KX_1^\infty = R
\]

So,

\[
\ln \left( \frac{KX_1 - KX_1^\infty}{KX_0 - KX_1^\infty} \right) = f \frac{KI}{V}, \quad \ln \left( \frac{X_1 - X_1^\infty}{X_0 - X_1^\infty} \right) = f \frac{KI}{V'}
\]

at the photostationary state,

\[
-V \frac{dC_1}{dt} = \phi_1 \frac{\epsilon_1 C_1}{D} I(1 - 10^{-D}) - \phi_2 \frac{\epsilon_2 C_2}{D} I(1 - 10^{-D}) = 0
\]

\[
\epsilon_1 \phi_1 X_1^\infty = \epsilon_2 \phi_2 X_2^\infty
\]

because \( K = \epsilon_1 \phi_1 + \epsilon_2 \phi_2 \),

\[
\phi_1 = K \frac{X_2^\infty}{\epsilon_1}, \quad \phi_2 = K \frac{X_1^\infty}{\epsilon_2}
\]  

(E6)

Quantum yield measurement

1. Extinction coefficients

The extinction coefficient at 355 and 457 nm for \textit{trans} isomers was measured by linear fitting of absorbance at a series of known concentrations of the pure compounds (Figure S18). The \textit{trans: cis} isomer ratio was determined by NMR integration of the PSS solution obtained by irradiation with a 355 nm laser. The extinction coefficient for \textit{cis} isomers at 355 nm and 457 nm is calculated using equation E7.

\[
\epsilon_{cis} = \frac{\epsilon_{pss} (\epsilon_{trans} X_1)}{(1 - X_1)}
\]  

(E7)

Where \( \epsilon_{pss} \) is the extinction coefficient of the mixture at the photostationary state, and \( X_1 \) is the fraction of \textit{trans} isomer in the mixture.
**Figure S18.** Extinction coefficients determined by linear fitting of absorbance vs concentration at 355 nm and 457 nm for both trans and cis isomers for 2 and 3.
2. Determination of constant $K$

Figure S19 shows the UV/vis absorption changes by conversion from trans to cis upon irradiation at 355 nm (left), and cis to trans upon irradiation at 457 nm (right) for compounds 2 and 3.

**Figure S19.** Changes in UV/vis absorbance for 2 (top) and 3 (bottom) under irradiation at 355 nm (left) and 457 nm (right).
According to the absorbance changes, the plot of $\ln\left(\frac{X_1 - X_1^\infty}{X_1^0 - X_1^\infty}\right)$ vs $f$ (Figure S20) was fitted to a linear equation to get the slope $\frac{Kf}{V}$ from equation (E5), then the constant $K$ can be calculated.

**Figure S20.** Constant $K$ determined by linear fitting of $\ln\left(\frac{X_1 - X_1^\infty}{X_1^0 - X_1^\infty}\right)$ with $f$ according to equation (E5).
3. Quantum yield

The quantum yields were calculated by equation (E6); results are listed in table S2.

**Table S2.** Extinction coefficients ($\varepsilon$) and quantum yields ($\Phi$) for 2 and 3

|       | Extinction coefficient $\varepsilon$ | Quantum Yield |       |
|-------|--------------------------------------|---------------|-------|
|       | trans  | cis | $\Phi_{E\rightarrow Z}$ ($\lambda_{irr}=355$ nm) | $\Phi_{Z\rightarrow E}$ ($\lambda_{irr}=457$ nm) |
| 2     | 355 nm | 18415.1 | 9016.3 | 0.164 | 0.598 |
|       | 457 nm | 1531.8 | 1415.5 |       |       |
| 3     | 355 nm | 20847.4 | 1775.1 | 0.110 | 0.469 |
|       | 457 nm | 835.5  | 1461.4 |       |       |
Thermal isomerization kinetics

Solutions of compounds 2, 3 and 4 were prepared in DMSO (UV-spectroscopy grade, ≥99.8%, Sigma-Aldrich) and diluted to the appropriate concentration (absorbance at λ_{max} between 1.2 – 1.5). The Z-enriched photostationary state was prepared from the pure E-isomer by irradiating the solution with a 355 nm laser with the cuvette inserted in the UV-Vis spectrometer equilibrated at the desired temperature. Irradiation was continued until no further spectral changes were observed (PSS reached). The thermal isomerization back to the E-isomers was subsequently followed by monitoring the spectral changes in time at several temperatures in the range of 45-105 °C. To minimize photochemical reactions during acquisition of spectra, the shutter was only opened during the measurement and a cut-off filter was used to remove wavelengths < 320 nm. Around 100 spectra were collected at each temperature covering full conversion back to the E-isomers. The final absorbance maximum was slightly sensitive to temperature, but indicated full conversion back to the E-isomers (instead of a photostationary state due to irradiation during the measurement). In addition, for several of the experiments the influence of sampling rate (= total exposure time to irradiation by the spectrometer) was checked to make sure that no competing photochemical conversion was taking place. All spectra were baseline-corrected (690-710 nm) using Spekwin32 (version 1.72.2) and the absorbance at 355 or 360 nm was extracted. The data were subsequently imported into Mathematica 10.3 for further analysis. For each compound, the data at different temperatures were normalized (absorption at 355 or 360 nm at the start set to 0; at complete conversion set to 1). A non-linear global fit of the data to the Eyring model was carried out, which resulted in the enthalpy and entropy of activation (ΔH^‡ and ΔS^‡, respectively). To evaluate the propagation of error due to uncertainty in the sample temperature, a Monte Carlo simulation of the data was carried out by adding a ‘temperature error’ chosen randomly from a standard distribution of 0.5 K around the temperature that was set for each measurement. In this way, 1000 simulated datasets were created to mimic an error of 0.5 K in the temperature. The activation parameters (ΔH^‡/ΔS^‡) are reported as the mean of this; the estimated error in the activation parameters is reported as the standard deviation for these values. The best fit parameters and estimated errors are given in Table S3; plots of the data for each individual compound are shown in Figures S21 – S24.

| compound | solvent | ΔH^‡ (kJ.mol^{-1}) | ΔS^‡ (J.mol^{-1}.K^{-1}) | ΔG^‡ (298 K) (kJ.mol^{-1}) | t_{1/2} (298 K) (days) |
|----------|---------|------------------|-----------------|------------------|-----------------|
| 2        | DMSO    | 100.0 ± 1.3      | -24 ± 4         | 107.1            | 7.7             |
| 2        | toluene | 97.6 ± 1.6       | -31 ± 5         | 106.8            | 6.8             |
| 3        | DMSO    | 96.9 ± 1.1       | -21 ± 3         | 103.3            | 1.6             |
| 4        | DMSO    | 99.2 ± 1.5       | -26 ± 4         | 107.0            | 7.3             |

Table S3. Activation parameters for thermal isomerization in compounds 2, 3 and 4.
Data for thermal $Z \rightarrow E$ isomerization for 2 in DMSO

**Figure S21a.** Normalized absorption vs time plots for 2; dots are measured data points, the lines represent the best (global) fit parameters. Data are shown up to 15000 s, but all reactions were followed to completion. Inset: corresponding Eyring plot with error bars (showing 20 σ(Ln[k])).

**Figure S21b.** Histogram for the global non-linear fit of $\Delta H^\ddagger$ (left, values on x-axis in kJ/mol) and $\Delta S^\ddagger$ (right, values on the x-axis in J/mol/K) for compound 2

**Table S4.** Rate constants for 2 in DMSO at various temperatures

| T (°C) | rate constant $(k \times 10^4 \text{ s}^{-1})$ | T (°C) | rate constant $(k \times 10^4 \text{ s}^{-1})$ | T (°C) | rate constant $(k \times 10^4 \text{ s}^{-1})$ |
|--------|-----------------------------------|--------|-----------------------------------|--------|-----------------------------------|
| 60     | 0.855                             | 80     | 6.695                             | 95     | 28.652                            |
| 70     | 2.341                             | 85     | 10.847                            | 100    | 44.593                            |
| 75     | 4.085                             | 90     | 17.732                            | 105    | 68.558                            |
Data for thermal \( Z \rightarrow E \) isomerization for 2 in toluene

Figure S22a. Normalized absorption vs time plots for 2 in toluene; dots are measured data points, the lines represent the best (global) fit parameters. Data are shown up to 15000 s, but all reactions were followed to completion. Inset: corresponding Eyring plot with error bars (showing 20 σ(Ln[k]).

Figure S22b. Histogram for the global non-linear fit of \( \Delta H^\ddagger \) (left, values on x-axis in kJ/mol) and \( \Delta S^\ddagger \) (right, values on the x-axis in J/mol/K) for compound 2 in toluene

Table S5. Rate constants for 2 in toluene at various temperatures

| T (°C) | rate constant \((k \times 10^4 \text{ s}^{-1})\) | T (°C) | rate constant \((k \times 10^4 \text{ s}^{-1})\) | T (°C) | rate constant \((k \times 10^4 \text{ s}^{-1})\) |
|--------|-----------------|--------|-----------------|--------|-----------------|
| 60     | 0.836           | 80     | 6.658           | 100    | 40.603          |
| 70     | 2.392           | 90     | 16.788          |        |                 |
Data for thermal $Z \rightarrow E$ isomerization for 3 in DMSO

**Figure S23a.** Normalized absorption vs time plots for 3; dots are measured data points, the lines represent the best (global) fit parameters. Data are shown up to 15000 s, but all reactions were followed to completion. Inset: corresponding Eyring plot with error bars (showing 20 σ(Ln[k])).

**Figure S23b.** Histogram for the global non-linear fit of $\Delta H^\ddagger$ (left, values on x-axis in kJ/mol) and $\Delta S^\ddagger$ (right, values on the x-axis in J/mol/K) for compound 3

**Table S6.** Rate constants for 3 in DMSO at various temperatures

| T (°C) | rate constant ($k \times 10^4$ s$^{-1}$) | T (°C) | rate constant ($k \times 10^4$ s$^{-1}$) | T (°C) | rate constant ($k \times 10^4$ s$^{-1}$) |
|-------|-----------------------------------------|-------|-----------------------------------------|-------|-----------------------------------------|
| 45    | 0.637                                   | 75    | 16.205                                  | 95    | 106.10                                  |
| 55    | 1.976                                   | 85    | 42.658                                  | 105   | 252.64                                  |
| 65    | 5.866                                   |       |                                         |       |                                         |
Data for thermal Z→E isomerization for 4 in DMSO

**Figure S24a.** Normalized absorption vs time plots for 4; dots are measure data points, the lines represent the best (global) fit parameters. Data are shown up to 15000 s, but all reactions were followed to completion. Inset: corresponding Eyring plot with error bars (showing 20 σ(Ln(k)).

**Figure S24b.** Histogram for the global non-linear fit of $\Delta H^\ddagger$ (left, values on x-axis in kJ/mol) and $\Delta S^\ddagger$ (right, values on the x-axis in J/mol/K) for compound 4

**Table S7.** Rate constants for 4 in DMSO at various temperatures

| $T$ (°C) | rate constant ($k \times 10^4$ s$^{-1}$) | $T$ (°C) | rate constant ($k \times 10^4$ s$^{-1}$) | $T$ (°C) | rate constant ($k \times 10^4$ s$^{-1}$) |
|----------|---------------------------------|----------|---------------------------------|----------|---------------------------------|
| 60       | 0.844                           | 85       | 11.024                          | 105      | 67.680                          |
| 75       | 4.052                           | 95       | 27.865                          |          |                                 |
Computational studies

Our main methodology relies on an implicit solvation picture based on the Polarizable Continuum Model (PCM)\(^8\) in combination with Density Functional Theory (DFT) and its Time-Dependent counterpart (TD) for electronic excited-states. All DFT/TD-DFT calculations were performed with the Gaussian software\(^9\) using the M06-2X\(^10\) exchange-correlation functional for geometry optimizations and thermodynamic calculations while PBE0\(^11\) functional was used for excited-state calculations. In all cases we applied a so-called *ultrafine* DFT integration grid (99,590 points). The TZVP atomic basis set\(^12\) was used for all calculations as a compromise between size and the accuracy. The optimized geometries and vibrational frequencies were obtained in toluene solvent and the perturbative corrected linear response (cLR) method\(^13\) was applied to determine the transition energies in the same solvent. The barrier for excited state rotation around the C-N(indazole) bond was obtained by constrained ES optimization at several values of this dihedral angle at PBE0 level. The angle C(mes)-N=N-C(ind) was fixed at its GS value to avoid collapse of the ES and GS, due to the barrierless pathway of photochromism.

Transition states for the *E* to *Z* isomerization involve breaking of a double bond, and to describe this phenomenon in a physically sound way, we have used broken-symmetry (BS) approach within DFT calculations. The transition state character of located minima was systematically confirmed by frequency calculation (one imaginary frequency found with value ca. 370i-430i cm\(^{-1}\)). Single-point energies were additionally calculated by CASPT2 (complete active space self-consistent field with second order multiconfigurational perturbation theory) with the TZVP atomic basis set. In CASPT2 we considered 16 electrons in 11 orbitals as an active space and used state-averaged wavefunction over the ground and the excited-states (equal weights) for excitation energies. Minimal active space for the compounds under study includes two combinations of lone pairs from aza nitrogen atoms and the π, π* orbitals for N=N bond. Using this active space in preliminary calculations, we build the final active space by adding the interacting π, π* orbitals having occupations inside the 0.05-1.95 interval, as well as orbitals close in energy to the minimal active space (see Figure S28). In the calculation of thermal activation energies, the focus is the ground-state only, and we optimized the corresponding wavefunction in a similar state-specific approach. Dynamical correlation effects were included using multi-state (MS) CASPT2 calculations, here the zero-order Hamiltonian was modified using a standard shift of 0.25 au.\(^14\) The Molcas software\(^15\) was used for multireference calculations. In order to speed up the calculations Cholesky decomposition of two-electron integrals was used with threshold 10\(^{-4}\) au.
### Table S8. Activation parameters for thermal isomerization in compounds 2, 3 and 4.

| Molecule | Mechanism         | $\Delta E^\ddagger$ (CASPT2) (kJ.mol$^{-1}$) | $\Delta E^\ddagger$ (M06-2X) (kJ.mol$^{-1}$) | $\Delta G^\ddagger$ (298 K) (kJ.mol$^{-1}$) | $\Delta S^\ddagger$ (J.mol$^{-1}$.K$^{-1}$) |
|----------|-------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|
| 2        | Mesitylene inversion | 154.7                                       | 131.1                                       | 123.8                                       | 4.9                                         |
|          | Indazole inversion | 142.1                                       | 131.4                                       | 126.9                                       | 10.2                                        |
|          | Rotation          | 137.1                                       | 110.9                                       | 103.8                                       | -10.0                                       |
| 3        | Benzene inversion  |                                            | 131.7                                       | 122.7                                       | 10.2                                        |
|          | Indazole inversion |                                            | 127.5                                       | 120.5                                       | 4.7                                         |
|          | Rotation          |                                            | 107.4                                       | 96.7                                        | -1.6                                        |
| 4        | Mesitylene inversion |                                            | 134.1                                       | 128.9                                       | -2.2                                        |
|          | Indazole inversion |                                            | 133.3                                       | 128.9                                       | -1.4                                        |
|          | Rotation          |                                            | 113.2                                       | 106.9                                       | -12.9                                       |
Table S9. Vertical excitation energies (VEE) and oscillator strengths calculated at PBE0 and CASPT2 levels of theory for the isomers of 2-5.

| Isomer-state | Oscillator strength f | TD-PBE0 VEE [nm] | CASPT2 VEE [nm] |
|--------------|-----------------------|------------------|-----------------|
| **2**        |                       |                  |                 |
| E1-S1        | 0.06                  | 468              | 443             |
| E1-S2        | 0.88                  | 350              | 279             |
| E2-S1        | 0.04                  | 500              | 475             |
| E2-S2        | 0.86                  | 370              | 308             |
| Z-S1         | 0.04                  | 479              | 428             |
| Z-S2         | 0.05                  | 340              | 270             |
| Z-S3         | 0.04                  | 337              | 258             |
| Z-S4         | 0.13                  | 328              | 262             |
| **3**        |                       |                  |                 |
| E1-S1        | 0.001                 | 452              |                 |
| E1-S2        | 0.81                  | 356              |                 |
| Z1-S1        | 0.05                  | 445              |                 |
| Z1-S2        | 0.12                  | 339              |                 |
| Z2-S1        | 0.04                  | 452              |                 |
| Z2-S2        | 0.08                  | 340              |                 |
| **4**        |                       |                  |                 |
| E1-S1        | 0.004                 | 481              |                 |
| E1-S2        | 0.70                  | 380              |                 |
| Z1-S1        | 0.05                  | 469              |                 |
| Z1-S2        | 0.12                  | 340              |                 |
|      | E₁-S₁ | 0.003 | 492 |
|------|-------|-------|-----|
|      | E₂-S₂ | 0.60  | 389 |
|      | Z₁-S₁ | 0.05  | 469 |
|      | Z₁-S₂ | 0.06  | 357 |
| Structure            | Figure | Relative ΔG (M06-2X/TZVP) [kJ/mol] |
|----------------------|--------|-----------------------------------|
| E₁-GS                | ![Image](image1.png) | 0.0                               |
| E₂-GS                | ![Image](image2.png) | 1.2                               |
| TS₁ (Rot)            | ![Image](image3.png) | 135.3                             |

**Figure S25.** Key isomers and transition states of molecule 2 and their relative free energy.
Figure S25 (continued). Key isomers and transition states of molecule 2 and their relative free energy.
Figure S26. Ground state energy profile for the indazole rotation around C-N(aza) bond as obtained with DFT
Figure S27. Singly occupied orbitals for the lowest excited states of the Z and $E$ isomers of 2 (TD-PBE0).
Figure S28. Molecular orbitals included in the active space during CAS calculation.
Presence of multiple rotamers: influence on quantum yields

The existence of multiple isomers of similar stabilities can influence the quantum yield of photo-isomerisation in two different ways. On the one hand, some of the excited-state "nuclear momentum" can be lost in the inter-conversion process. We therefore calculated the barrier for the inter-conversion between the two rotamers in the excited state, and this barrier is relatively low (16 kJ/mol). Therefore, this rotational pathway is potentially open in the excited-state which can lead to a loss of energy and, possibly, more effective non-radiative vibrational deactivation. On the other hand, each rotamer could in principle proceed via a different photochemical pathway (in an extreme case, only one of the two could be photochemically active, which would obviously be detrimental for the photochemical conversion). Therefore, we investigated this aspect as well and we found that, for both rotamers, a barrierless pathway to a specific conical intersection exists. This pathway mainly involves the rotation around C(mes)-N=N-C(ind)dihedral angle. Having made these two observations, we can conclude that the CI route should be favored over the rotamer inter-conv (barrierless process versus small barrier), though of course some small amount of excited-state interconversion could still appear as a minority process. Therefore, photochemical transformation of the E$_1$-2 rotamer will lead to Z$_1$-2 rotamer and analogously E$_2$-2 to Z$_2$-2. Since Z$_2$-2 is more stable (14 kJ/mol difference) and as the barrier for Z$_1$-2 $\rightarrow$ Z$_2$-2 rotation is small (6 kJ/mol) on the ground-state surface, the final equilibrium will be dominated by Z$_2$. The total quantum yield is therefore mainly influenced by the non-radiative pathways and the efficiencies of each conical intersection explored by the system, rather than by excited-state rotameric interconversions. We expect comparable photochemical efficiencies for both isomers, based on the structural similarity and same character of the first excited-state. Quantitative modeling of the QY would require excited-state dynamics, but due to the size of the systems investigated here, this is beyond reasonable reach. Recently, Thiel and coworkers studied chiral pathways for the excited relaxation in arylazopyrazole switches where the barrier is as small as 2 kJ/mol.$^{16}$ Such small barrier was found to significantly penalize one of the chiral excited-state relaxations. This supports our conclusion that for our systems each rotamer will relax by its own conical intersection without significant mutual transformations in excited state. In short, the observed rather small quantum yield can be the result of the flexible structure of the switch allowing vibrational relaxation of the excited-state but none of the described rotamers blocks the photoreaction.
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