

## Electronic Supplementary Information (13 pages, including title page)

### An acido- and photochromic molecular device that mimics triode action

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## 1. Materials and methods

The synthesis and analytical characterization of compound **1** (counterion bromide) is described in a previous work.<sup>1</sup>

All experiments were performed in aqueous solution at 25 °C. For pH 3.0 to 8.0 the solutions were buffered with Na<sub>2</sub>HPO<sub>4</sub>/NaH<sub>2</sub>PO<sub>4</sub> buffers (10 mM) and at pH 1.5 the solution was set by adding standard portions of concentrated HCl. The buffers for pH 3.0 to 8.0 were prepared by mixing different proportions of Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub> and then were adjusted by adding NaOH (0.1 M) or HCl (0.1 M).

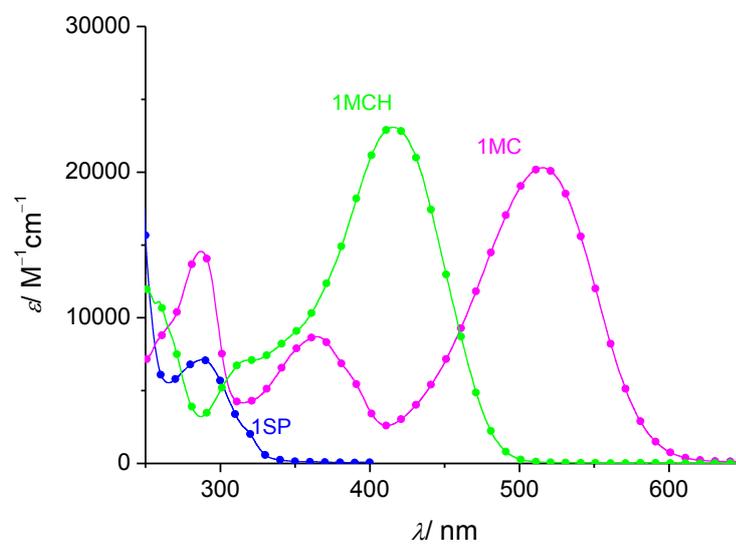
The UV/vis absorption measurements were carried out on a CaryBio 50 spectrometer. The UV light used to initiate the photochromic reactions was generated by a UVP lamp, model UVGL-25 ( $\lambda = 254$  nm, 700  $\mu\text{W}/\text{cm}^2$ ). The irradiation time was 8 min for full UV intensity and 60 min for the attenuated intensity (attenuation to 1.3% of full intensity). The thermal equilibrium was established within 4 and 5 hours depending on the pH of the solution.

The UV/vis absorption spectra of the different forms of **1** (**1SP**, **1MC**, **1MCH**) were determined as follows. The SP form was available from the synthesis and green light irradiation was employed to the aqueous solution at pH 7 to assure the exclusive presence of the ring-closed form. The thermally stable MCH form was generated by thermal equilibration of **1SP** in acidic solution for 18 h. The latter solution was then set to pH 7 and measured quickly before notable thermal ring closure of the thus generated MC form back to SP was observed.

The quantum yields for the isomerisation reactions **1SP**→**1MC** and **1MC**→**1SP** were reported in a previous work.<sup>2</sup> The corresponding value for the decolorisation reaction **1MCH**→**1SP** was determined with the same procedure as published before,<sup>2</sup> employing the decolorisation reaction of the furylfulgide 2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride as actinometric reference.<sup>3-6</sup> While the quantum yields for the decolorisation reactions (**1MC**→**1SP** and **1MCH**→**1SP**) were measured for visible-light irradiation, they can be assumed to be wavelength independent and therefore applicable to the irradiation conditions used in the present work (254 nm).

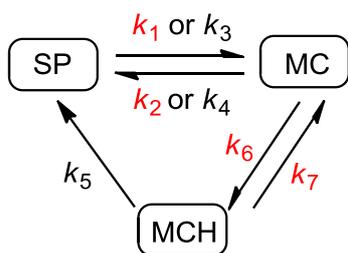
For the reported rate constants it should be noted that these are apparent rate constants as they depend on the reaction conditions.<sup>7</sup>

## 2. UV/vis absorption spectra of 1SP, 1MC, and 1MCH



**Figure S1.** UV/vis absorption spectra of **1SP**, **1MC** (both at pH 7), and **1MCH** (at pH 2) in aqueous solution.

### 3. Modelling of the switch network



**Scheme S1.** Generalized scheme with all relevant thermal and light-induced (photochromic) processes for the pH range 1.5–8. The kinetic constants referring to the thermal processes are shown in red and the ones referring to the UV-induced processes are in black.

The rate constants  $k_1$ – $k_5$  were determined experimentally; see below. The rate constants  $k_6$  and  $k_7$  were varied as to reflect the correct  $[MC]/[MCH]$  ratio at each pH, given the  $pK_a$ -value of 4.4. Due to the fast pH-equilibration,  $k_6$  and  $k_7$  were set to several orders of magnitude faster than all other rate constants.

The modelling was performed by application of Laplace transformation analysis.<sup>8</sup>

#### 3.1. Laplace transformation analysis of the thermally induced processes (dark reactions, no UV irradiation)



**Scheme S2.** Kinetic constants of the thermal processes

*Initial conditions:*

$$[SP]_0 = a$$

$$[MC]_0 = 0$$

$$[MCH]_0 = 0$$

Equations:

$$[\text{SP}] = a \left( \frac{k_2 k_7}{\gamma_1 \gamma_2} - \frac{k_1 (\gamma_1 - k_6 - k_7)}{\gamma_1 (\gamma_2 - \gamma_1)} e^{-\gamma_1 t} - \frac{k_1 (k_6 + k_7 - \gamma_2)}{\gamma_2 (\gamma_2 - \gamma_1)} e^{-\gamma_2 t} \right)$$

$$[\text{MC}] = a k_1 \left( \frac{k_7}{\gamma_1 \gamma_2} + \frac{k_7 - \gamma_1}{\gamma_1 (\gamma_1 - \gamma_2)} e^{-\gamma_1 t} + \frac{k_7 - \gamma_2}{\gamma_2 (\gamma_2 - \gamma_1)} e^{-\gamma_2 t} \right)$$

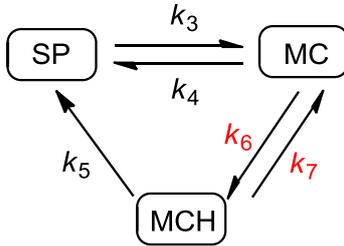
$$[\text{MCH}] = a k_1 k_6 \left( \frac{1}{\gamma_1 \gamma_2} + \frac{1}{\gamma_1 (\gamma_1 - \gamma_2)} e^{-\gamma_1 t} - \frac{1}{\gamma_2 (\gamma_1 - \gamma_2)} e^{-\gamma_2 t} \right)$$

where:

$$\gamma_1 \gamma_2 = k_2 k_7 + k_1 k_6 + k_1 k_7$$

$$\gamma_1 + \gamma_2 = k_1 + k_2 + k_6 + k_7$$

### 3.2. Laplace transformation analysis for irradiation with full UV intensity



**Scheme S3.** Kinetic constants of the pH-dependent (thermal) and UV-induced processes. The kinetic constants referring to the thermal processes are shown in red and the ones referring to the UV-induced processes are in black.

Initial conditions:

$$[\text{SP}]_0 = a$$

$$[\text{MC}]_0 = 0$$

$$[\text{MCH}]_0 = 0$$

Equations:

$$[\text{SP}] = a \left( \frac{\beta}{\gamma_1 \gamma_2} + \frac{\alpha \gamma_1 - \gamma_1^2 - \beta}{\gamma_2 - \gamma_1} e^{-\gamma_1 t} + \frac{\gamma_2^2 - \alpha \gamma_2 + \beta}{\gamma_2 - \gamma_1} e^{-\gamma_2 t} \right)$$

$$[\text{MC}] = a \left( \frac{\varepsilon}{\gamma_1 \gamma_2} + \frac{k_3 \gamma_1 - \varepsilon}{\gamma_2 - \gamma_1} e^{-\gamma_1 t} + \frac{\varepsilon - k_3 \gamma_2}{\gamma_2 - \gamma_1} e^{-\gamma_2 t} \right)$$

$$[\text{MCH}] = a \left( \frac{\delta}{\gamma_1 \gamma_2} - \frac{\delta}{\gamma_2 - \gamma_1} e^{-\gamma_1 t} + \frac{\delta}{\gamma_2 - \gamma_1} e^{-\gamma_2 t} \right)$$

where:

$$\alpha = k_4 + k_6 + k_7 + k_5$$

$$\beta = k_4 k_7 + k_4 k_5 + k_6 k_5$$

$$\varepsilon = k_3 k_7 + k_3 k_5$$

$$\delta = k_3 k_6$$

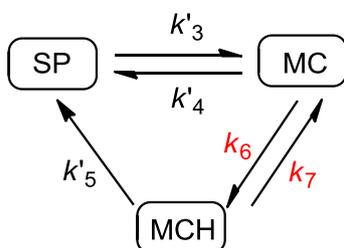
$$\gamma_1 \gamma_2 = \beta + \varepsilon + \delta$$

$$\gamma_1 + \gamma_2 = \alpha + k_3$$

### 3.3. Laplace transformation analysis for irradiation with attenuated UV intensity

When the intensity of the UV light is attenuated the rate constants of the photochromic processes are, of course, smaller. This results in a more pronounced participation of the thermal processes in the overall equilibrium establishment (thermal and UV-induced).

In order to modulate this scenario by a Laplace transformation analysis<sup>8</sup> the chosen model was the one shown in Scheme S4.



**Scheme S4.** Kinetic constants of the overall equilibrium establishment using the attenuated UV-intensity.

The rate constants  $k_3'$  and  $k_4'$  correspond to the sum of the respective rate constants of the thermal and the UV-induced processes at attenuated intensity.

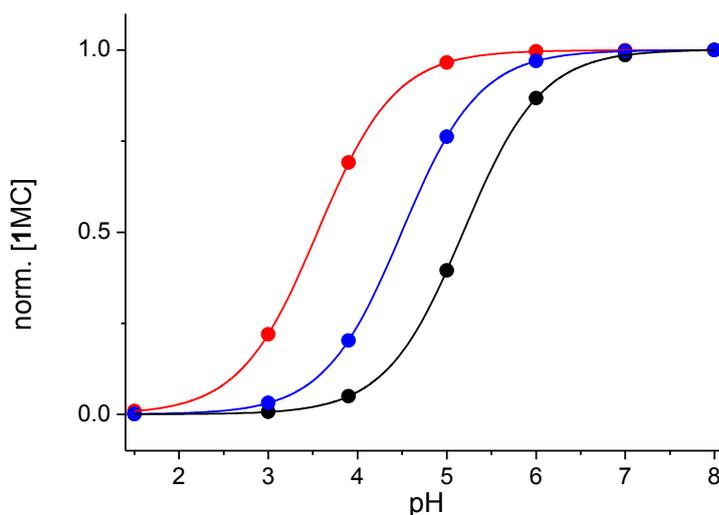
$$k_3' = k_1 + k_3 \cdot I/100$$

$$k_4' = k_2 + k_4 \cdot I/100$$

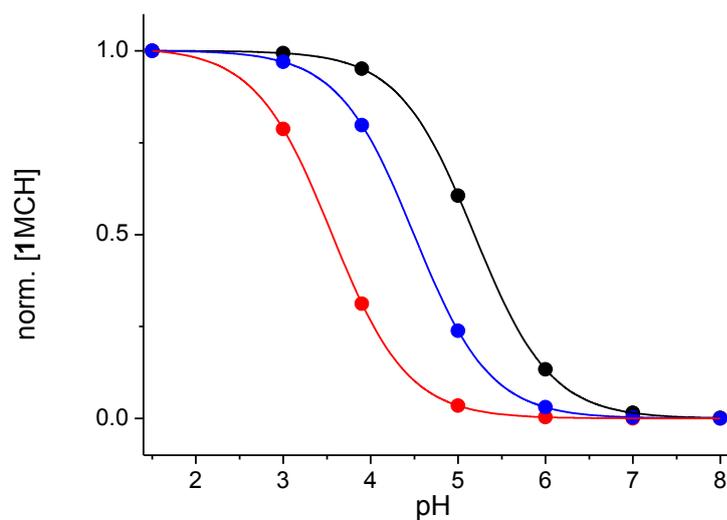
$$k_5' = k_5 \cdot I/100$$

where  $I$  is the attenuated UV intensity (in % of the full UV-intensity). These re-defined rate constants were used in Laplace transformation analysis as shown above for irradiation with full UV intensity.

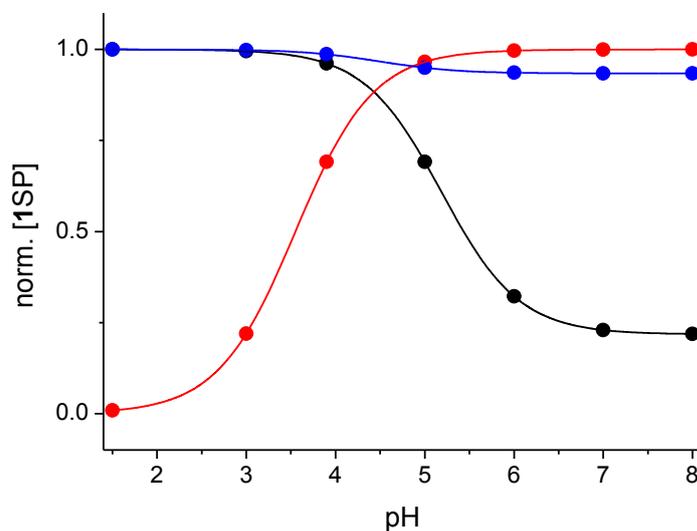
### Modelling results:



**Figure S2.** Modelled pH curves showing the normalised 1MC concentration ( $[1MC]/[1MC]_{\max}$ ). Colour codes: red = absence of irradiation (dark reaction); black = UV irradiation at full intensity; blue = irradiation with an attenuated UV intensity (to 1.3%). The lines correspond to sigmoid fits for guiding the eye.



**Figure S3.** Modelled pH curves showing the normalised **1MCH** concentration ( $[\mathbf{1MCH}]/[\mathbf{1MCH}]_{\max}$ ). Colour codes: red = absence of irradiation (dark reaction); black = UV irradiation at full intensity; blue = irradiation with an attenuated UV intensity (to 1.3%). The lines correspond to sigmoid fits for guiding the eye.



**Figure S4.** Modelled pH curves showing the normalised **1SP** concentration ( $[\mathbf{1SP}]/[\mathbf{1SP}]_{\max}$ ). Colour codes: red = absence of irradiation (dark reaction); black = UV irradiation at full intensity; blue = irradiation with an attenuated UV intensity (to 1.3%). The lines correspond to sigmoid fits for guiding the eye.

#### 4. Experimental determination of $k_1$ – $k_5$

The rate constants for thermal equilibration ( $k_1 = 5.6 \times 10^{-3} \text{ min}^{-1}$  and  $k_2 = 3.4 \times 10^{-2} \text{ min}^{-1}$ ) were taken from a previous work.<sup>2</sup>

*Determination of  $k_3$  and  $k_4$ :*

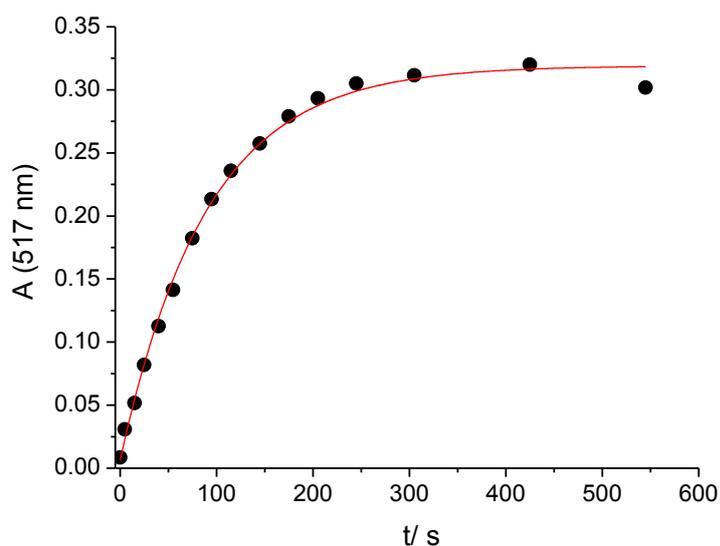
$$k_3 + k_4 = 1/\tau_{\text{isomerization}}$$

$$k_3/k_4 = 4.3 \text{ (photostationary state distribution; [1MC]/[1SP])}$$

$$\tau_{\text{isomerization}} = 1.49 \text{ min}$$

$$k_3 = 5.45 \times 10^{-1} \text{ min}^{-1}$$

$$k_4 = 1.27 \times 10^{-1} \text{ min}^{-1}$$

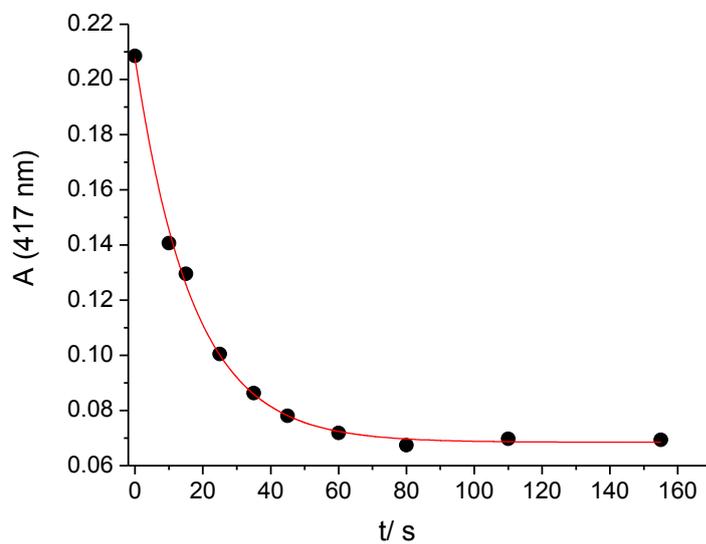


**Figure S5.** UV/vis absorption changes (517 nm) on irradiation of **1SP** at 254 nm ( $700 \mu\text{W}/\text{cm}^2$ ); pH 7. The red line corresponds to a monoexponential fit.

Determination of  $k_5$ :

$$\tau = 0.28 \text{ min}$$

$$k_5 = 3.56 \text{ min}^{-1}$$



**Figure S6.** UV/vis absorption changes (417 nm) on irradiation of **1MCH** at 254 nm ( $700 \mu\text{W}/\text{cm}^2$ ); pH 2. The red line corresponds to a monoexponential fit.

## 5. Calculation of the concentration of SP, MC, and MCH from the experimental absorption measurements at different pH values

[SP], [MC], and [MCH] at any pH between 1.5 and 8 were calculated as follows:

If:

$$1) [SP]_0 = [MC] + [MCH] + [SP] \text{ (material balance)}$$

$$2) A_{515(\text{exptl})} = \varepsilon_{515,MC} \cdot [MC] \text{ (only MC absorbs at 515 nm)}$$

$$3) A_{416(\text{exptl})} = \varepsilon_{416,MC} \cdot [MC] + \varepsilon_{416,MCH} \cdot [MCH] \text{ (SP does not absorb at 416 nm)}$$

then:

$$[MC] = \frac{A_{515(\text{exptl})}}{\varepsilon_{515,MC}^{MC}}$$

and

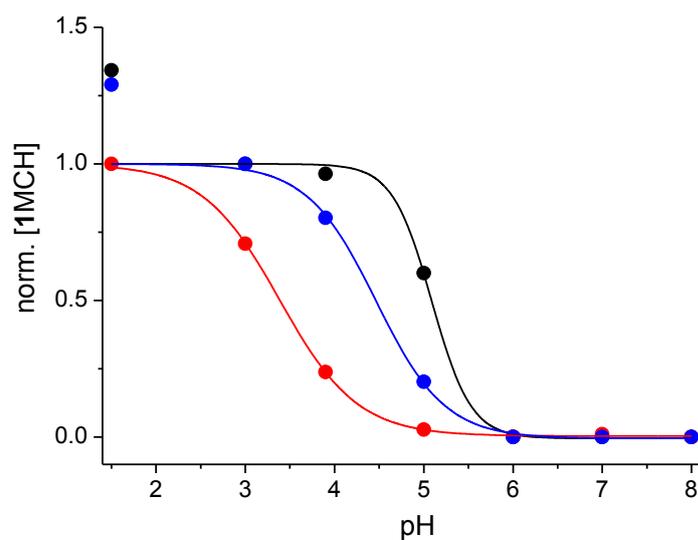
$$A_{416(\text{exptl})} = \varepsilon_{416,MC} \cdot \frac{A_{515(\text{exptl})}}{\varepsilon_{515,MC}} + \varepsilon_{416,MCH} \cdot [MCH]$$

and

$$[MCH] = \frac{A_{416(\text{exptl})} - \varepsilon_{416,MC} \cdot \frac{A_{515(\text{exptl})}}{\varepsilon_{515,MC}}}{\varepsilon_{416,MCH}}$$

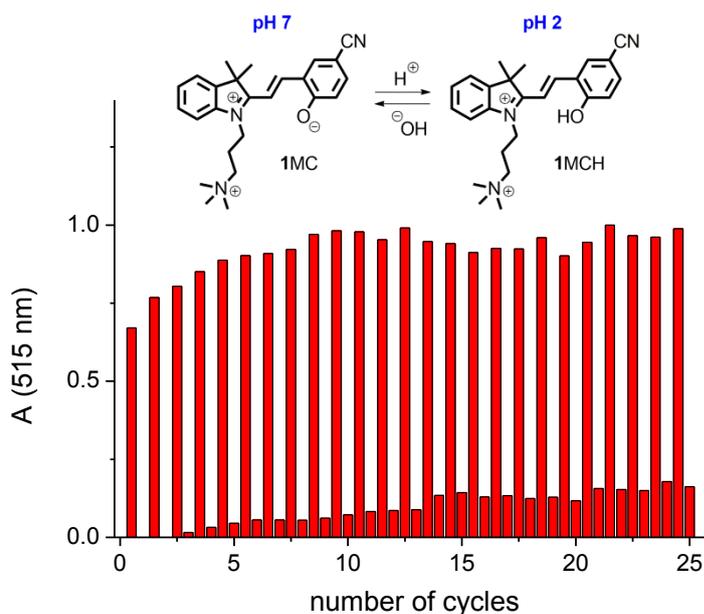
and

$$[SP] = [SP]_0 - \frac{A_{416(\text{exptl})} - \varepsilon_{416,MC} \cdot \frac{A_{515(\text{exptl})}}{\varepsilon_{515,MC}}}{\varepsilon_{416,MCH}} - \frac{A_{515(\text{exptl})}}{\varepsilon_{515,MC}}$$



**Figure S7.** pH titration curves monitoring the normalised **1MCH** concentration ( $[\mathbf{1MCH}]/[\mathbf{1MCH}]_{\max}$ ) in the dark (red), under UV irradiation at full intensity (254 nm; black) or attenuated UV irradiation (to 1.3% of full intensity; blue). The data were obtained under equilibrium conditions (i.e., thermal equilibrium and/or PSS). The sigmoid curves are meant to guide the eye. For pH = 1.5 outlier were produced for the irradiated samples.

## 6. Recycling experiment



**Figure S8.** A solution of **1SP** (19.7  $\mu\text{M}$ ) at pH = 7 (phosphate buffer) was left in darkness until reaching the thermal equilibrium. Subsequently alternate additions of trifluoroacetic acid and NaOH were used to toggle the solution pH between 7 and 2. Dilution effects were kept to a minimum.

## 7. References

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