# Photoinduced pH drops in water

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## **Suuporting Information Available**

The Supporting Information reports on:

- The NMR spectra of the **P** and **THPCl<sub>3</sub>** polymers.
- The spectrophotometric titrations.
- The proton exchange constants of the trans 2-hydroxy-azobenzenes (including Figure 2S);
- The kinetic analysis of the photochemical behavior of 2-hydroxy-azobenzenes (comprising the theory and the experimental results; including Schemes 1–2S and Figures 3–5S);
- The thermodynamic model evaluating the amplitude of the photoinduced pH drop;
- The evaluation of the fatigue of the 2-hydroxyazobenzene platform in water (including Figure 6S).

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# NMR spectra of polymers P and THPCl<sub>3</sub>



**Figure 1S.** NMR spectra of **P** in D<sub>2</sub>O (**a**) and **THPCl<sub>3</sub>** in DMSO d<sub>6</sub> (**b**). Concentrations  $\approx$  5 mg/mL. T = 298 K.





**Figure 2S.** Evolution of absorption spectra as a function of pH. **a**: 40 μM **THSO<sub>3</sub>KCl<sub>3</sub>** in BR (pH = 1.7, 4.5, 6.3, 6.9, 7.1, 7.7, 8.0, 8.6, 9.5); **b**: 76 μM **THSO<sub>3</sub>KCl<sub>3</sub>** in BR–acetonitrile 75–25 (v/v) (pH = 2.0, 6.7, 7.2, 7.8, 8.2, 8.7, 9.3); **c**: 51 μM **THSO<sub>3</sub>KCl<sub>3</sub>** in BR–acetonitrile 1–1 (v/v) (pH = 6.5, 7.6, 8.4, 9.0, 9.8,

10.4, 11.2, 11.7); **d**: 7  $\mu$ M **TH**<sub>2</sub>**Cl**<sub>3</sub> in 30 mM octyl– $\beta$ –D–glucopyranoside in BR (pH = 2.5, 3.3, 4.9, 5.8, 6.8, 7.7, 8.4, 9.7, 10.2, 11.3, 11.9, 12.3); **e**: 40  $\mu$ M **TH**<sub>2</sub>**Cl**<sub>3</sub> in 62 mM CTAC in BR (pH = 1.8, 2.4, 3.5, 4.3, 4.8, 5.6, 6.4, 7.0, 8.2, 9.0, 9.5, 10.7, 11.2); **f**: 60  $\mu$ M **THPCl**<sub>3</sub> in BR (pH = 2.0, 5.1, 7.2, 8.0, 8.2, 8.8, 9.1, 9.4, 9.8, 10.3, 10.9). T = 298 K.

Figure 2S displays the evolution of the absorption spectra of the various substrates investigated in the present study as a function of the proton concentration expressed by its pH assuming  $pH = -log_{10} H$  where H designates the proton concentration. Each individual collection of absorption spectra was globally fitted to extract the thermodynamic proton exchange constant of the trans stereoisomer of the considered 2-hydroxy-azobenzenes. The results are given in the Main Text. The global fit also provides the spectra of the acidic and basic states of the trans stereoisomers of the 2-hydroxy-azobenzenes. Table 1S sums up their main photophysical features.

**Table 1S.** Maximal wavelengths of absorption and molar absorption coefficients for the acidic  $(\lambda_{\text{max}}^{\text{TH}}[\varepsilon(\lambda_{\text{max}}^{\text{TH}})])$ and basic  $(\lambda_{\text{max}}^{\text{T}}[\varepsilon(\lambda_{\text{max}}^{\text{T}})])$  states of the investigated 2-hydroxy-azobenzene systems. BR: Britton-Robinson buffer<sup>2</sup> (acetic acid, boric acid, phosphoric acid; 0.04 M). T = 298 K.

Molecule	BR-CH <sub>3</sub> CN (v-v)	Additive	$ \begin{array}{c} \lambda_{max}^{TH}[\epsilon(\lambda_{max}^{TH})] \\ (nm)[mM^{-1}cm^{-1}] \end{array} $	$ \begin{array}{c} \lambda_{\max}^{\mathbf{T}}[\boldsymbol{\varepsilon}(\lambda_{\max}^{\mathbf{T}})] \\ (nm)[mM^{-1}cm^{-1}] \end{array} $
THSO <sub>3</sub> KCl <sub>3</sub>	100-0	$\oslash$	348[19]	451[4]
THSO <sub>3</sub> KCl <sub>3</sub>	75-25	$\oslash$	349[21]	450[5]
THSO <sub>3</sub> KCl <sub>3</sub>	50-50	$\oslash$	349[22] <sup><i>a</i></sup>	451[6] <sup><i>a</i></sup>
TH <sub>2</sub> Cl <sub>3</sub>	100-0	OG	348[18]	460–520[≈3] <sup>b</sup>
TH <sub>2</sub> Cl <sub>3</sub>	100-0	CTAC	351[15]	449[6]
TH <sub>2</sub> Cl <sub>3</sub>	50-50	$\oslash$	347[20] <sup><i>a</i></sup>	435[5] <sup><i>a</i></sup>
THPCI <sub>3</sub>	100-0	$\oslash$	353[16]	445[3]
<sup><i>a</i></sup> Data from <sup>1</sup>				

<sup>&</sup>lt;sup>b</sup> Shoulder

# Kinetic analysis of the photochemical behavior of 2-hydroxyazobenzenes

## Theory

#### The model

We are here interested to derive the theoretical expressions of the concentrations in **TH**, **T**, **CH** and **C** (TH, T, CH, and C respectively) during the illumination.

We first assume that the system (volume V) is homogeneous at any time of its evolution. In particular, the whole system is not homogeneously illuminated during the quantitative irradiation experiments; only part of the system (volume  $V_{exc}$ ) is submitted to light. Thus matter transport has to be considered to support the homogeneity assumption. In our experiments, the cuvette content is continuously stirred and the homogeneity assumption is fulfilled as soon as the photochemical evolution does not occur much below the second time scale which is here the case. Thus the following equations can be considered as valid beyond a characteristic homogeneization time scale by considering concentrations averaged over the whole volume V.



Scheme 1S. Mechanism accounting for the photochemical behavior of 2-hydroxy-azobenzenes.

Then we rely on the mechanism displayed in Scheme 1S to write Eqs.(1–4) describing the concentration evolutions:

$$\frac{dTH}{dt} = -(k_{\mathbf{TH}\to\mathbf{T}} + k_{\mathbf{TH}\to\mathbf{CH}}) TH + k_{\mathbf{CH}\to\mathbf{TH}} CH + k_{\mathbf{T}\to\mathbf{TH}} H T$$
(1)

$$\frac{dCH}{dt} = k_{\text{TH}\to\text{CH}} TH - (k_{\text{CH}\to\text{C}} + k_{\text{CH}\to\text{TH}}) CH + k_{\text{C}\to\text{CH}} H C$$
(2)

$$\frac{dT}{dt} = k_{\mathbf{TH}\to\mathbf{T}}TH - (k_{\mathbf{T}\to\mathbf{TH}}H + k_{\mathbf{T}\to\mathbf{C}})T + k_{\mathbf{C}\to\mathbf{T}}C$$
(3)

$$\frac{dC}{dt} = k_{\mathbf{CH}\to\mathbf{C}}CH + k_{\mathbf{T}\to\mathbf{C}}T - (k_{\mathbf{C}\to\mathbf{CH}}H + k_{\mathbf{C}\to\mathbf{T}})C$$
(4)

where we make explicit the photochemical and thermal contributions to the rate constants by writing

$$k_{\mathbf{C}\to\mathbf{T}} = k_{\mathbf{C}\to\mathbf{T}}^{h\nu} + k_{\mathbf{C}\to\mathbf{T}}^{\Delta}$$
(5)

$$k_{\mathbf{CH}\to\mathbf{TH}} = k_{\mathbf{CH}\to\mathbf{TH}}^{h\nu} + k_{\mathbf{CH}\to\mathbf{TH}}^{\Delta}$$
(6)

$$k_{\mathrm{TH}\to\mathrm{CH}} = k_{\mathrm{TH}\to\mathrm{CH}}^{h\nu}$$
(7)

$$k_{\mathbf{T}\to\mathbf{C}} = k_{\mathbf{T}\to\mathbf{C}}^{h\nu} \tag{8}$$

where the exponent indicates the nature of the contribution.

Then we take into account that the exchange between **TH** and **T** (**CH** and **C** respectively) is fast at the time scale of the observed photochemical evolution; beyond the relaxation times associated to proton exchanges, it is meaningful to introduce the average species  $\overline{T}$  and  $\overline{C}$  (concentrations  $\overline{T} = TH + T$  and  $\overline{C} = CH + C$ ). Under such a condition, the "instantaneous" concentrations in **TH**,

#### T, CH and C are respectively

$$TH = \frac{H}{H + K_{\rm TH}}\overline{T} \tag{9}$$

$$T = \frac{K_{\rm TH}}{H + K_{\rm TH}}\overline{T}$$
(10)

$$CH = \frac{H}{H + K_{\rm CH}}\overline{C} \tag{11}$$

$$C = \frac{K_{\rm CH}}{H + K_{\rm CH}}\overline{C}$$
(12)

where  $K_{\text{TH}}$  and  $K_{\text{CH}}$  designate the proton exchange thermodynamic constants associated to **TH** and **CH**). Thus Eqs.(1–4) transform into Eq.(13):

$$\frac{d\overline{T}}{dt} = -\frac{d\overline{C}}{dt} = -k_{\overline{T}\to\overline{C}}\overline{T} + k_{\overline{C}\to\overline{T}}\overline{C}$$
(13)

with

$$k_{\overline{\mathbf{T}}\to\overline{\mathbf{C}}} = \frac{k_{\mathbf{T}\to\mathbf{C}}K_{\mathbf{TH}} + k_{\mathbf{TH}\to\mathbf{CH}}H}{H + K_{\mathbf{TH}}}$$
(14)

$$k_{\overline{\mathbf{C}}\to\overline{\mathbf{T}}} = \frac{k_{\mathbf{C}\to\mathbf{T}}K_{\mathbf{CH}} + k_{\mathbf{CH}\to\mathbf{TH}}H}{H + K_{\mathbf{CH}}}$$
(15)

Considering that the initial concentrations in  $\overline{\mathbf{T}}$  and  $\overline{\mathbf{C}}$  are  $\overline{T}_0$  and  $\overline{C}_0$  respectively, Eq.(13) eventually provides

$$\overline{T} = \frac{1}{1+K_{\overline{\mathbf{T}}\to\overline{\mathbf{C}}}} \left(\overline{T}_0 + \overline{C}_0\right) + \left(\frac{K_{\overline{\mathbf{T}}\to\overline{\mathbf{C}}}}{1+K_{\overline{\mathbf{T}}\to\overline{\mathbf{C}}}} \overline{T}_0 - \frac{1}{1+K_{\overline{\mathbf{T}}\to\overline{\mathbf{C}}}} \overline{C}_0\right) \exp\left[-\left(k_{\overline{\mathbf{T}}\to\overline{\mathbf{C}}} + k_{\overline{\mathbf{C}}\to\overline{\mathbf{T}}}\right)t\right] (16)$$

$$\overline{C} = \frac{K_{\overline{\mathbf{T}}\to\overline{\mathbf{C}}}}{1+K_{\overline{\mathbf{T}}\to\overline{\mathbf{C}}}} \left(\overline{T}_0 + \overline{C}_0\right) - \left(\frac{K_{\overline{\mathbf{T}}\to\overline{\mathbf{C}}}}{1+K_{\overline{\mathbf{T}}\to\overline{\mathbf{C}}}} \overline{T}_0 - \frac{1}{1+K_{\overline{\mathbf{T}}\to\overline{\mathbf{C}}}} \overline{C}_0\right) \exp\left[-\left(k_{\overline{\mathbf{T}}\to\overline{\mathbf{C}}} + k_{\overline{\mathbf{C}}\to\overline{\mathbf{T}}}\right)t\right] (17)$$

with  $K_{\overline{T}\to\overline{C}} = k_{\overline{T}\to\overline{C}}/k_{\overline{C}\to\overline{T}}$ . The concentrations in **TH**, **T**, **CH** and **C** can eventually be derived from Eqs.(9–12) and Eqs.(16–17).

#### Application to the measurement of the CH proton exchange thermodynamic constants

In the following series of experiments, the **TH** solution is first illuminated with the spectrofluorimeter lamp to generate a photo-steady state in which **TH**, **T**, **CH**, and **C** are present at concentration  $TH_0$ ,  $T_0$ ,  $CH_0$ , and  $C_0$ . The illuminated sample is then transferred to the dark and the kinetics of thermally-driven cis-to-trans isomerization is analyzed by following the sample absorbance as a function of time.<sup>1</sup> The temporal evolution of the concentrations  $\overline{T}$  and  $\overline{C}$  obeys Eq.(13) which here reduce to

$$\overline{T} = \overline{T}_0 + \overline{C}_0 \left[ 1 - \exp\left(-k_{\overline{\mathbf{C}} \to \overline{\mathbf{T}}}^{\Delta} t\right) \right]$$
(18)

$$\overline{C} = \overline{C}_0 \exp\left(-k\frac{\Delta}{\overline{C}} - \overline{T}t\right)$$
(19)

with

$$k_{\overline{\mathbf{C}}\to\overline{\mathbf{T}}}^{\Delta} = \frac{k_{\overline{\mathbf{C}}\to\mathbf{T}}^{\Delta}K_{\mathbf{CH}} + k_{\mathbf{CH}\to\mathbf{TH}}^{\Delta}H}{H + K_{\mathbf{CH}}}$$
(20)

The observed absorbance A is the sum of the contribution from  $\overline{\mathbf{T}}$  and  $\overline{\mathbf{C}}$ 

$$A = \left[ \varepsilon_{\overline{\mathbf{T}}} \left( \overline{T}_0 + \overline{C}_0 \right) + \overline{C}_0 \left( \varepsilon_{\overline{\mathbf{C}}} - \varepsilon_{\overline{\mathbf{T}}} \right) \exp\left( -k_{\overline{\mathbf{C}} \to \overline{\mathbf{T}}}^{\Delta} t \right) \right] \ell$$
(21)

at the chosen wavelength. Fitting the temporal dependence of the absorbance *A* with Eq. (21) yields  $k_{\overline{C}\to\overline{T}}^{\Delta}$  at a given pH. After repeating the latter experiment with appropriate proton concentrations, the fit of the dependence of  $k_{\overline{C}\to\overline{T}}^{\Delta}$  on proton concentration *H* with Eq.(20) provides:  $K_{CH}$ ,  $k_{CH\to TH}^{\Delta}$ , and  $k_{C\to T}^{\Delta}$ .

<sup>&</sup>lt;sup>1</sup>The power of the UV-Vis lamp for absorbance measurement is too low to introduce any significant perturbation during the measurement of  $k_{\overline{C}\to\overline{T}}^{\Delta}$  since  $k_{\overline{C}\to\overline{T}}^{\Delta} \gg k_{\overline{C}\to\overline{T}}^{hv}$ .

## **Experimental results**

#### Observations of "slow" cis-to-trans thermal isomerizations

When the cis-to-trans thermal isomerization was slow enough (for  $TH_2Cl_3$  and  $THPCl_3$ ), we had time to transfer to the spectrophotometer the cuvette containing the **TH** solution illuminated up to the photo-steady state in order to analyze the kinetics of the thermal relaxation toward the initial state by following the sample absorbance as a function of time. Figure 3Sa displays the relaxation at 298 K of a pH = 4.7 **THPCl<sub>3</sub>** solution which has been illuminated for 5 min at 365 nm and which are typical of the results obtained with  $TH_2Cl_3$  and  $THPCl_3$ . The relaxation occurs at the 30 s timescale and it is satisfactorily accounted for by the kinetic model.



**Figure 3S. a**: Temporal evolution of the absorbance at 353 nm of a 60  $\mu$ M **THPCl<sub>3</sub>** solution in pH 4.7 BR after irradiation at 365 nm for 5 min. From the fit with Eq. (21), we extracted  $k_{\overline{C}\to\overline{T}}^{\Delta}(pH = 4.7) = 3.8 \pm 0.1$  min<sup>-1</sup>; **b**: Temporal evolution of the transmitted light intensity at 365 nm I(365) of a 50  $\mu$ M **THSO<sub>3</sub>KCl<sub>3</sub>** solution in pH 6.7 BR after irradiation at 365 nm for 5 min. From the fit with Eq. (22), we extracted  $k_{\overline{C}\to\overline{T}}^{\Delta}(pH = 6.7) = 12\pm2$  min<sup>-1</sup>. Markers: experimental data; solid lines: fits. T = 298 K.

#### Observations of "fast" cis-to-trans thermal isomerizations

For **THSO<sub>3</sub>KCl<sub>3</sub>**, the cis-to-trans thermal isomerization occurred too fast to be analyzed with the procedure explained above. To overcome this limitation, we modified our fluorimeter to illuminate the sample and record its transmittance in a same setup (Scheme 2S).



Scheme 2S. Schematic view of the modified fluorimeter cavity. The light emitted from the low intensity 365 nm light source (UV diode; Nichia chip UV LED NCSU033A(T), 0–700 mA) passes through the sample and the intensity of the transmitted light (I(365)) is recorded by the photomultiplier (PM) set up at 365 nm while irradiating with the lamp of the fluorimeter (arc lamp).

In order to validate our set up, two experiments have been done.

• Firstly we checked that the UV diode delivering  $I_0(365)$  was weak enough so as to not perturb the system, *i.e.* to not cause any significant trans-to-cis photo-isomerization. Thus we exposed to the light from the UV diode for 5 min a 5  $10^{-4}$  M **TH**<sub>2</sub>**Cl**<sub>3</sub> solution in pH 7.8 BR– acetonitrile 1–1 (v/v). The solution was subsequently transferred to the spectrophotometer in which we recorded the transmittance at the maximal absorption wavelength of the solution (347 nm) as a function of time. Since we did not observe any significant variation of the recorded signal at the timescale of the relaxation time for the thermal cis-to-trans isomerization (around 300 s at pH 7.8<sup>1</sup>), we deduced that there was no isomerization induced by the light coming from the UV diode. • Secondly, we measured the cis-to-trans thermal rate constants for  $\mathbf{TH}_2\mathbf{Cl}_3$  in pH 7.8 BR– acetonitrile 1–1 (v/v), both in the spectrophotometer (as explained above) and in the modified fluorimeter. A 5 10<sup>-4</sup> M  $\mathbf{TH}_2\mathbf{Cl}_3$  solution was illuminated at 347 nm for 5 min with the arc lamp of the fluorimeter and the thermal cis-to-trans isomerization was subsequently either observed in the spectrophotometer (Figure 4Sa) or in the modified fluorimeter (Figure 4Sb). Fitting the temporal evolution of A(365) as in Figure 3Sa yielded  $k_{\overline{C}\to\overline{T}}^{\Delta} = 3.7 \pm 0.1 \ 10^{-3} \ s^{-1}$ whereas the fit of the temporal evolution of I(365) with the equation<sup>2</sup>

$$I(365) = I_0(365) \exp\left[-\frac{\ell}{\alpha} \left(\varepsilon_{\overline{\mathbf{T}}}(\overline{T}_0 + \overline{C}_0) + \overline{C}_0(\varepsilon_{\overline{\mathbf{C}}} - \varepsilon_{\overline{\mathbf{T}}}) \exp(-k_{\overline{\mathbf{C}} \to \overline{\mathbf{T}}}^{\Delta}t)\right)\right]$$
(22)

which was extracted from Eqs. (18), (19), and (21) gave  $k_{\overline{C}\to\overline{T}}^{\Delta} = 3.5 \pm 0.1 \ 10^{-3} \ s^{-1}$ . From the fair agreement between both values, we concluded that our instrumental set up was relevant for analyzing "fast" cis-to-trans thermal isomerizations with the relation  $A(365) = \alpha \log \frac{I_0(365)}{I(365)}$  ( $\alpha$  is a geometrical parameter) linking the sample absorbance at 365 nm, A(365), and the PM signal, I(365).



**Figure 4S.** Relaxation of an illuminated 5  $10^{-4}$  M solution of **TH**<sub>2</sub>**Cl**<sub>3</sub> in pH 7.8 BR–acetonitrile 1–1 (v/v) that has been illuminated at 347 nm by the arc lamp for 5 min in the fluorimeter and was subsequently

<sup>&</sup>lt;sup>2</sup>The absence of baseline/dark signal correction of the transmitted light intensity was guided by our choice to analyze only its temporal dependence in order to extract the rate constant  $k_{\overline{C}\to\overline{T}}^{\Delta}$ . As evidenced by Eq.(22), any additional contribution will not affect the temporal dependence governed by  $k_{\overline{C}\to\overline{T}}^{\Delta}$ .

observed by recording its absorbance at 365 nm, A(365) with the spectrophotometer (**a**) or its transmittance at 365 nm, I(365), with the fluorimeter (**b**). Dots : experimental points, lines : fits with Eq. (21) (**a**) and Eq. (22) (**b**).  $T = 25^{\circ}C$ .

Figure 3Sb displays the relaxation at 298 K of a pH = 6.7 **THSO<sub>3</sub>KCl<sub>3</sub>** solution which has been illuminated for 5 min at 365 nm which are typical of the results obtained with **THSO<sub>3</sub>KCl<sub>3</sub>**. The relaxation occurs at the 5 s timescale and it is satisfactorily accounted for by the kinetic model.

Derivations of the proton exchange constant of the cis 2-hydroxy-azobenzenes and of the rate constants of cis-to-trans thermal isomerizations



**Figure 5S.** Dependence of the rate constant  $k_{\overline{C}\to\overline{T}}^{\Delta}$  as a function of pH. **a**: **THSO<sub>3</sub>KCl<sub>3</sub>** in BR; **b**: **TH<sub>2</sub>Cl<sub>3</sub>** in 30 mM octyl– $\beta$ –D–glucopyranoside in BR; **c**: **TH<sub>2</sub>Cl<sub>3</sub>** in 62 mM CTAC in BR; **d**: **THPCl<sub>3</sub>** in BR. Markers: experimental data; solid lines: fits with Eq.(20). T = 298 K.

Figure 5S shows that the dependence of the rate constants  $k_{\overline{C}\to\overline{T}}^{\Delta}$  on the proton concentration is in line with the predicted behavior given in Eq.(20) for all the investigated compounds. The fits of the experimental data yielded  $pK_{CH}$  and  $k_{CH\to TH}^{\Delta}$  given in the Main Text. In fact, the last  $k_{C\to T}^{\Delta}$ estimate extracted from the fit noticeably lacked precision as the relaxation becomes very slow at the highest pH. Therefore, we relied on the linear temporal evolution of the absorbance at pH=8 beyond 60 min to deduce that the actual value of the rate constants  $k_{C\to T}^{\Delta}$  were lower than 3 10<sup>-2</sup> min<sup>-1</sup> for all the investigated 2-hydroxy azobenzenes.

# Thermodynamic model evaluating the amplitude of the photoinduced pH drop

In this section, we introduce a thermodynamic model to evaluate the dependence of the amplitude of **TH** photoinduced pH drops on control parameters.

We consider that at initial pH, only **TH** (proton exchange constant  $K_{TH}$ ) exists in the system. Under UV illumination, **TH** is transformed into **CH** (proton exchange constant  $K_{CH}$ ) yielding a photostationary state containing both species. We want to address the amplitude of the pH modification between the nonilluminated initial system and the photostationary state.

## Proton concentration in the nonilluminated starting system

We first calculate the proton concentration  $H_{\text{dark}}$  resulting from thermal ionization of the nonilluminated photoacid **TH** at thermodynamic equilibrium:

$$TH = T + H^+$$

Neglecting solvent self-ionization and assuming that the concentration in **TH**,  $TH_{tot}$ , is sufficiently large, we find

$$H_{\text{dark}} = \sqrt{K_{\text{TH}}TH_{\text{tot}}}.$$
(23)

### Proton concentration in the photostationary state

We now calculate the proton concentration in the photostationary state  $H_{\text{photostat}}$  containing both **TH** and **CH**. Considering that the proton exchange constant of **CH** is much higher than the one of **TH** (see Table 1 in Main Text), we assume that the proton concentration in the photostationary state is only controlled by the **CH** dissociation thermodynamic equilibrium:

$$CH = C + H^+$$

Consequently the proton concentration in the photostationary state  $H_{\text{photostat}}$  is easily obtained from the proton exchange constant of **CH** (*K***<sub>CH</sub>**) and the photostationary concentration of **CH** (*CH*) :

$$H_{\rm photostat} = \sqrt{K_{\rm CH}CH}.$$
(24)

The concentration of **CH** is ruled by Eq.(13) taking into account Eqs.(9–12). Assuming that the photostationary concentrations of **TH** and **CH** are large enough and that **TH** and **CH** are weak acids, we neglect the concentration *T* in front of *TH* (respectively *C* in front of *CH*) and write  $\overline{T} \approx TH, \overline{C} \approx CH$  and  $TH_{\text{tot}} \approx TH + CH$  to derive

$$\frac{CH}{TH} = \frac{k_{\text{TH}} \to \text{CH}}{k_{\text{CH}} \to \text{TH}}$$
(25)

with  $k_{\text{TH}\rightarrow\text{CH}} = k_{\text{TH}\rightarrow\text{CH}}^{h\nu}$  and  $k_{\text{CH}\rightarrow\text{TH}} = k_{\text{CH}\rightarrow\text{TH}}^{h\nu} + k_{\text{CH}\rightarrow\text{TH}}^{\Delta}$  where the irradiation-driven rate constants obey :

$$k_{\mathbf{TH}\to\mathbf{CH}}^{h\nu} = \varepsilon_{\mathbf{TH}} \phi_{\mathbf{TH}\to\mathbf{CH}} \frac{1 - \exp(-2.3A_{\text{tot}})}{A_{\text{tot}}V} I_0$$
(26)

$$k_{\mathbf{CH}\to\mathbf{TH}}^{h\nu} = \varepsilon_{\mathbf{CH}} \phi_{\mathbf{CH}\to\mathbf{TH}} \frac{1 - \exp(-2.3A_{\text{tot}})}{A_{\text{tot}}V} I_0$$
(27)

where  $\varepsilon_{\text{TH}}$  and  $\varepsilon_{\text{CH}}$  are the absorption coefficients of **TH** and **CH** at the irradiation wavelenght;  $\phi_{\text{TH}}$  and  $\phi_{\text{CH}}$  the quantum yields of the photoisomerization reactions **TH**  $\rightarrow$  **CH** and **CH**  $\rightarrow$  **TH**; *V* the irradiated volum,  $A_{\text{tot}}$  the total absorbance of the solution and  $I_0$  the light intensity.

Then we get

$$CH = \frac{1}{1 + \frac{k_{\text{CH}} - \text{TH}}{k_{\text{TH}} - \text{CH}}} TH_{\text{tot}}.$$
(28)

From Eqs.(24) and (28), we eventually obtain

$$H_{\text{photostat}} = \sqrt{K_{\text{CH}} \frac{1}{1 + \frac{k_{\text{CH}} \rightarrow \text{TH}}{k_{\text{TH}} \rightarrow \text{CH}}} T H_{\text{tot}}}.$$
(29)

Hence we deduce the amplitude of the photogenerated pH drop ( $\Delta pH = pH_{\text{photostat}} - pH_{\text{dark}}$ )

using Eqs.(23) and (29) and the relation  $pH = -log_{10}H$ 

$$\Delta pH = -log_{10}H_{\text{photostat}} + log_{10}H_{\text{dark}} = \frac{1}{2}\left[\left(pK_{\text{CH}} - pK_{\text{TH}}\right) + log_{10}\left(1 + \frac{k_{\text{CH}} - \text{TH}}{k_{\text{TH}} - \text{CH}}\right)\right]$$
(30)

Some key features accounting for the amplitude of the **TH** photoinduced pH drop can be extracted from Eq.(30) :

- $pK_{CH} pK_{TH}$ . The largest protonation constant enhancement of the photoacid **TH** upon illumination, the largest resulting *pH* drop;
- k<sub>CH→TH</sub>/k<sub>TH→CH</sub>. In relation to Eq.(25), the largest CH concentration at steady-state, the largest resulting *pH* drop. Consequently, the pH drop amplitude increases with light intensity. However when light intensity becomes large enough (k<sup>hv</sup><sub>CH→TH</sub> >> k<sup>Δ</sup><sub>CH→TH</sub>), the pH drop saturates. In the present case, the typical light intensity delimitating both regims is 10<sup>-7</sup> Ei.s<sup>-1</sup>.
- $TH_{tot}$ . In contrast to  $pH_{drak}$  and  $pH_{photostat}$ ,  $\Delta pH$  does not depend on the total photoacid concentration  $TH_{tot}$ .

# Evaluation of the fatigue of the 2-hydroxyazobenzene platform

# in water

In order to prove that the 2-hydroxyazobenzene platform do not feature any significant fatigue after several illuminations, we submitted aqueous solutions of the photoacids to several switching cycles in which we alternated UV illumination and darkness.

Figure 6S displays the resulting pH variations after eight (240  $\mu$ M TH<sub>2</sub>Cl<sub>3</sub> 50 mM CTAC 200 mM NaCl; **a**) and four (340  $\mu$ M THPCl<sub>3</sub>; **b**) cycles in water.



**Figure 6S.** pH variations of a 240  $\mu$ M **TH<sub>2</sub>Cl<sub>3</sub>** 50 mM CTAC 200 mM NaCl solution submitted to eight photocycles (**a**) and of a 340  $\mu$ M **THPCl<sub>3</sub>** solution submitted to four photocycles (**b**). The light pulses are at 365 nm and 1.2 10<sup>-5</sup> Einstein s<sup>-1</sup> with a flux of 1.7 10<sup>-6</sup> Einstein s<sup>-1</sup> cm<sup>-2</sup>. Red arrows: light is switched off. T = 298 K.

# References

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