Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for:
Large Protonation-Gated Photochromism of an OPE-Embedded Difurylperfluorocyclopentene

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1. System of equations for calculating the equilibrium concentrations of the species B, BH$^+$, BH_2^{2+}, HA and A$^-$

Here the symbol B for the base applies to either of the photochromic forms **S$_o$** and **S$_c$**.

$$\frac{\left[A^-\right][BH^+]}{[B]} = 2K_1[HA] \tag{S1}$$

$$\frac{\left[A^-\right][BH_2^{2+}]}{[BH^+]} = K_2[HA] \tag{S2}$$

$$[B]_0 = [B] + \left[BH^+\right] + [BH_2^{2+}] \tag{S3}$$

$$[HA]_0 = \left[HA\right] + [A^-] \tag{S4}$$

$$\left[HA\right]_0 = \left[HA\right] + \left[BH^+\right] + 2\left[BH_2^{2+}\right] \tag{S5}$$

2. Absorbance/Absorbance diagrams for the spectral change on titration of S$_o$ by TFAH

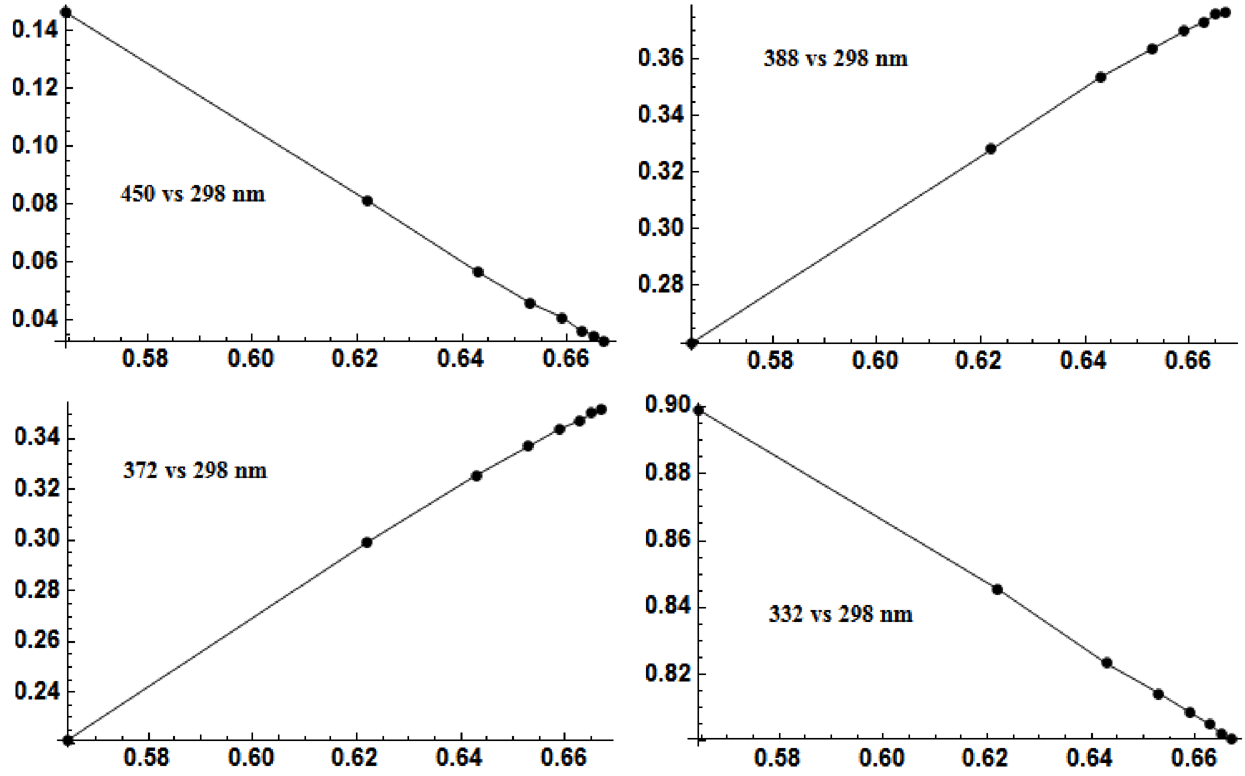

Figure S1 Absorbance vs. absorbance diagrams for the wavelengths of strongest spectral change during titration of **S$_o$** by TFAH (cf. Spectra in Figure 1).

3. Simulated spectra of the three protolytic forms

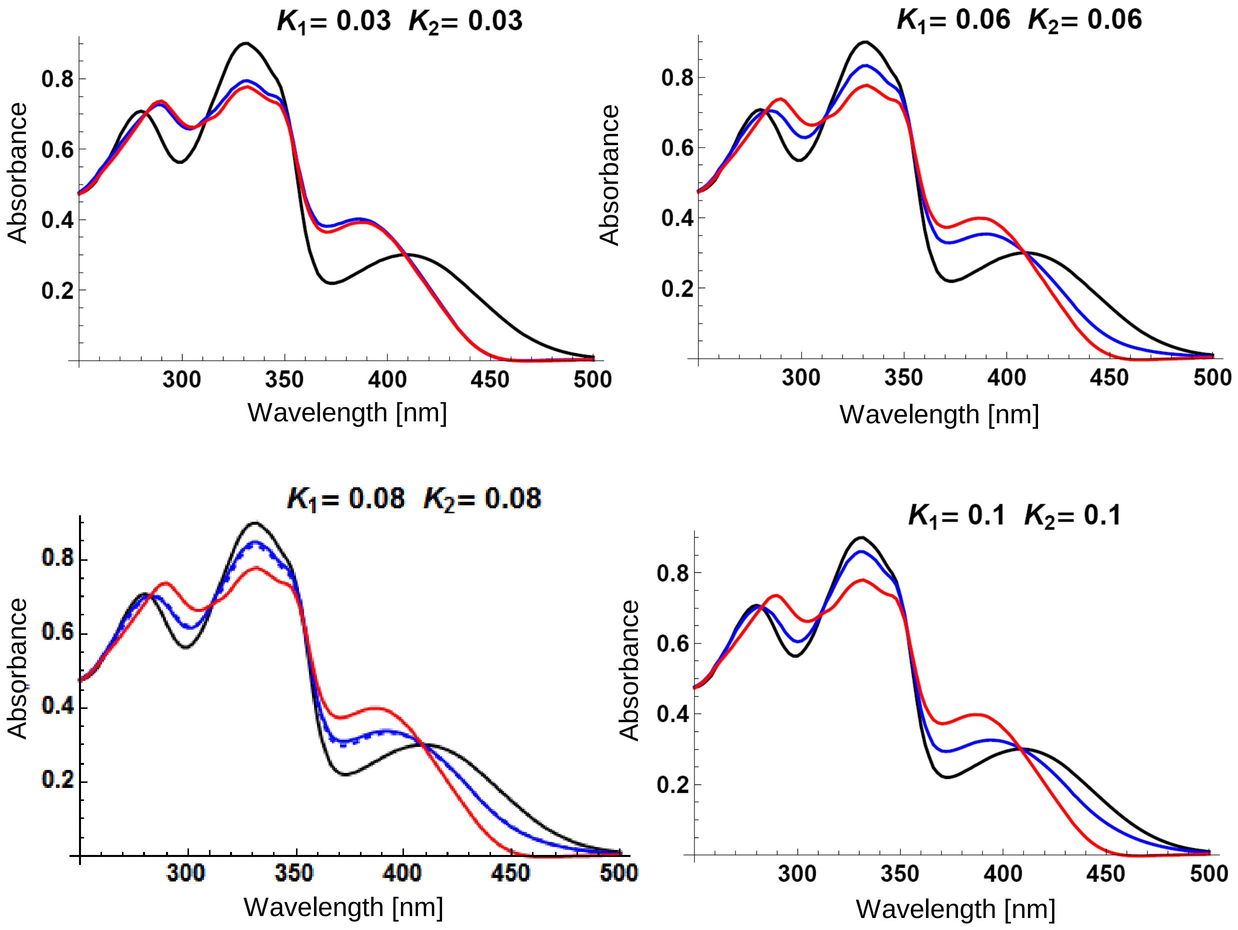

Figure S2 Simulated spectra of the three protolytic forms $\mathbf{S_o}$ (black), $\mathbf{S_o}H^+$ (blue) and $\mathbf{S_o}H_2^{2+}$ (red) for representative values of the equilibrium constants K_1 and K_2. In all cases, the fit of $A_\lambda([TFAH]_0)$ is equally good. In case of the fit values $K_1 = K_2 = 0.08$ the spectrum of BH^+ is best centered between those of B and BH_2^{++}. In this case it is also shown that the spectrum of $\mathbf{S_o}H^+$ is close to a linear combination of the spectra of $\mathbf{S_o}$ and $\mathbf{S_o}H_2^{2+}$ (dashed blue curve).

4. Defining a $pH_{non\text{-}aq}$ for a non-aqueous aprotic solvent

In water, protolytic equilibria are related to solvated protons H^+_{aq} , usually written as H_3O^+, but often just denoted H^+. For example for a general base B

$$B + H^+ \overset{K_B}{\rightleftarrows} BH^+ \tag{S6}$$

According to the law of mass action, the equilibrium concentrations of B and BH^+ are determined by the equilibrium constant K_B and the proton concentration $[H^+]$:

$$\frac{\left[\mathrm{BH}^{+}\right]}{[\mathrm{B}]}=K_B[\mathrm{H}^{+}]=K_B\times 10^{-pH} \tag{S7}$$

The acidity or protonating power of the solution is described by the pH defined as:

$$pH_{aq}=-\log\left[\mathrm{H}^{+}\right] \tag{S8}$$

In non-aqueous aprotic solvents that cannot be protonated, the protons are donated by the undissociated acid:

$$\mathrm{B}+\mathrm{HA}\overset{K_B}{\rightleftarrows}\mathrm{BH}^{+}+\mathrm{A}^{-} \tag{S9}$$

Hence the ratio of equilibrium concentrations of B and BH^+ is given by:

$$\frac{\left[\mathrm{BH}^{+}\right]}{[\mathrm{B}]}=K_B\frac{[\mathrm{HA}]}{[\mathrm{A}^{-}]} \tag{S10}$$

Consequently, for a given acid HA, the acidity in a non-aqueous aprotic solvent may be defined by the ratio $[\mathrm{HA}]/[\mathrm{A}^-]$. Hence the systematic generalization of the definition of pH for a non-aqueous aprotic solvent containing the acid HA would be:

$$pH_{non-aq}=-\log\frac{[\mathrm{HA}]}{[\mathrm{A}^{-}]} \tag{S11}$$

and the concentration ratio of acid to base form is again uniquely determined by $\mathrm{pH}_{\text{non-aq}}$.

$$\frac{\left[\mathrm{BH}^{+}\right]}{[\mathrm{B}]}=K_B\times 10^{-pH_{non-aq}} \tag{S12}$$

This concept is similar to the Hammet H_0 function in superacid media.[S1,S2]

5. Calculation of fractions of protolytic forms during forward and back titration

In the following, base B represents either of the two photochromic forms $\mathbf{S_o}$ and $\mathbf{S_c}$ with its specific equilibrium constants**.** The definitions:

$$b_1\equiv\frac{[\mathrm{BH}^{+}]}{[\mathrm{B}]}=2K_1 10^{-pH} \tag{S13}$$

$$b_2\equiv\frac{[\mathrm{BH}_2^{2+}]}{[\mathrm{BH}^{+}]}=K_2 10^{-pH} \tag{S14}$$

are useful to represent the fractions of the various protolytic forms:

$$X\equiv\frac{[\mathrm{B}]}{[\mathrm{B}]_{\mathrm{tot}}}=\frac{1}{1+b_1+b_1b_2} \tag{S15}$$

$$Y\equiv\frac{[\mathrm{BH}^{+}]}{[\mathrm{B}]_{\mathrm{tot}}}=\frac{b_1}{1+b_1+b_1b_2} \tag{S16}$$

$$Z\equiv\frac{[\mathrm{BH}_2^{2+}]}{[\mathrm{B}]_{\mathrm{tot}}}=\frac{b_1b_2}{1+b_1+b_1b_2} \tag{S17}$$

Note that, depending on the case, the concentration $[\mathrm{B}]_{tot}$ refers to $[\mathbf{S_o}]_{tot}$ or $[\mathbf{S}_\mathrm{c}]_{tot}$. Using these fractions, the absorbance at any wavelength is represented as:

$$A(\lambda, pH) = A_1(\lambda)\,X + A_2(\lambda)\,\mathrm{Y} + A_3(\lambda)\,Z \qquad \text{(S18)}$$

with the definitions

$$A_1 = \varepsilon_B \ell [B]_{tot} \qquad A_2 = \varepsilon_{BH^+} \ell [B]_{tot} \qquad A_3 = \varepsilon_{BH_2^{2+}} \ell [B]_{tot} \qquad \text{(S19)}$$

where the ε_i represent the molar extinctions coefficients of the various species and ℓ the optical path length.

6. Derivations of the pH dependent quantum yields of individual protolytic forms

The time-dependence of the sum $[\mathbf{S_o}]_{tot}$ of the concentrations of the open forms is described by equation ((S20)):

$$\begin{aligned}\frac{d[\mathrm{S}_\mathbf{o}]_{tot}}{dt} = I_0 \frac{F}{V}\left(1-10^{-A}\right)\Bigg\{ & -\Phi_{\mathrm{S}_o} \frac{\varepsilon_{\mathrm{S}_o} \ell [\mathrm{S}_\mathbf{o}]}{A} - \Phi_{\mathrm{S_oH^+}} \frac{\varepsilon_{\mathrm{S_oH^+}} \ell \left[\mathrm{S}_\mathbf{o}\mathrm{H}^+\right]}{A} - \Phi_{\mathrm{S}_o\mathrm{H}_2^{2+}} \frac{\varepsilon_{\mathrm{S}_o\mathrm{H}_2^{2+}} \ell \left[\mathrm{S}_\mathbf{o}\mathrm{H}_2^{2+}\right]}{A} \\ & + \Phi_{\mathrm{S}_c} \frac{\varepsilon_{\mathrm{S}_c} \ell [\mathrm{S}_\mathbf{c}]}{A} + \Phi_{\mathrm{S}_c\mathrm{H}^+} \frac{\varepsilon_{\mathrm{S}_c\mathrm{H}^+} \ell [\mathrm{S}_\mathbf{c}\mathrm{H}^+]}{A} + \Phi_{\mathrm{S}_c\mathrm{H}_2^{2+}} \frac{\varepsilon_{\mathrm{S}_c\mathrm{H}_2^{2+}} \ell \left[\mathrm{S}_\mathbf{c}\mathrm{H}_2^{2+}\right]}{A} \Bigg\}\end{aligned} \qquad \text{(S20)}$$

where I_0 is the photon flux density, *F* the illuminated area of the cuvette, *V* the (stirred) volume of the sample solution, *A* the total absorbance at the wavelength of irradiation, the various ε parameters the molar absorption coefficients of the respective species, and ℓ the optical path length. Using the definitions in S**ection 5** above and the expression for the photokinetic factor F_{pk}

$$F_{pk} = \frac{A}{1-10^{-A}} \qquad \text{(S21)}$$

equation (S20) can be simplified to:

$$\begin{aligned}\frac{d[\mathrm{S}_\mathbf{o}]_{tot}}{dt} = -F_{pk}^{-1} I_0 \frac{F}{V} \Big\{ & \left(\Phi_{\mathrm{S}_o} A_{o,1} X_o + \Phi_{\mathrm{S_oH^+}} A_{o,2} Y_o + \Phi_{\mathrm{S}_o\mathrm{H}_2^{2+}} A_{o,3} Z_o\right) [\mathbf{S_o}]_{tot} \\ & - \left(\Phi_{\mathrm{S_c}} A_{c,1} X_c + \Phi_{\mathrm{S}_c\mathrm{H}^+} A_{c,2} Y_c + \Phi_{\mathrm{S}_c\mathrm{H}_2^{2+}} A_{c,3} Z_c\right) [\mathbf{S_c}]_{tot} \Big\}\end{aligned} \qquad \text{(S22)}$$

Substituting $[\mathbf{S_c}]_{\mathrm{tot}}$ by:

$$[\mathbf{S_c}]_{\mathrm{tot}} = [\mathbf{S}]_{\mathrm{tot}} - [\mathbf{S_o}]_{\mathrm{tot}} \qquad \text{(S23)}$$

yields:

$$\begin{aligned}\frac{d[\mathrm{S}_\mathbf{o}]_{tot}}{dt} = -F_{pk}^{-1} I_0 \frac{F}{V} \Big\{ & \left(\Phi_{\mathrm{S}_o} A_{o,1} X_o + \Phi_{\mathrm{S_oH^+}} A_{o,2} Y_o + \Phi_{\mathrm{S_oH_2^{2+}}} A_{o,3} Z_o + \Phi_{\mathrm{S_c}} A_{c,1} X_c + \Phi_{\mathrm{S_cH^+}} A_{c,2} Y_c + \Phi_{\mathrm{S}_c\mathrm{H}_2^{2+}} A_{c,3} Z_c\right) [\mathbf{S_o}]_{tot} \\ & - \left(\Phi_{\mathrm{S_c}} A_{c,1} X_c + \Phi_{\mathrm{S}_c\mathrm{H}^+} A_{c,2} Y_c + \Phi_{\mathrm{S}_c\mathrm{H}_2^{2+}} A_{c,3} Z_c\right) [\mathbf{S}]_{tot} \Big\}\end{aligned}$$

$$\text{(S24)}$$

Within each kinetic run at a given $\mathrm{pH}_{\text{non-aq}}$, the expressions in the round brackets of equation (S24) are constant. They represent the analogues of the pseudo quantum yield Q in a photoreversible reaction with one protolytic species only. Defining

$$\begin{aligned} Q &= \vec{Q} + \overleftarrow{Q} \\ &= \left(\Phi_{\mathrm{S}_o} A_{o,1} X_o + \Phi_{\mathrm{S}_o\mathrm{H}^+} A_{o,2} Y_o + \Phi_{\mathrm{S}_o\mathrm{H}_2^{2+}} A_{o,3} Z_o \right) + \left(\Phi_{\mathrm{S}_c} A_{c,1} X_c + \Phi_{\mathrm{S}_c\mathrm{H}^+} A_{c,2} Y_c + \Phi_{\mathrm{S}_c\mathrm{H}_2^{2+}} A_{c,3} Z_c \right) \end{aligned} \quad \text{(S25)}$$

with

$$\vec{Q} = \Phi_{\mathrm{S}_o} A_{o,1} X_o + \Phi_{\mathrm{S}_o\mathrm{H}^+} A_{o,2} Y_o + \Phi_{\mathrm{S}_o\mathrm{H}_2^{2+}} A_{o,3} Z_o \quad \text{(S26)}$$

$$\overleftarrow{Q} = \Phi_{\mathrm{S}_c} A_{c,1} X_c + \Phi_{\mathrm{S}_c\mathrm{H}^+} A_{c,2} Y_c + \Phi_{\mathrm{S}_c\mathrm{H}_2^{2+}} A_{c,3} Z_c \quad \text{(S27)}$$

the photokinetic rate law simplifies to:

$$\frac{d\left[\mathbf{S_o}\right]_{tot}}{dt} = -F_{pk}^{-1} I_0 \frac{F}{V} \left\{ Q[\mathbf{S_o}]_{tot} - \overleftarrow{Q}[\mathbf{S}]_{tot} \right\} \quad \text{(S28)}$$

The second term in parentheses is related to the PSS by:

$$\overleftarrow{Q}[\mathbf{S}]_{tot} = Q[\mathbf{S_o}]_{tot,pss} \quad \text{(S29)}$$

Thus, equation (S28) can be written as

$$\frac{d\left[\mathbf{S_o}\right]_{o,tot}}{dt} = -F_{pk}^{-1} I_0 \frac{F}{V} Q \left\{ [\mathbf{S_o}]_{tot} - [\mathbf{S_o}]_{tot,pss} \right\} \quad \text{(S30)}$$

Since $\left[\mathbf{S_o}\right]_{o,tot}$ is linearly related to the absorbance at any wavelength, an equation of the form of equation (S30) is also valid for the absorbance *A* at the observation wavelength of choice:

$$\frac{dA}{dt} = -F_{pk}^{-1} I_0 \frac{F}{V} Q \left\{ A - A_{pss} \right\} \quad \text{(S31)}$$

Resolving equation (S29) for $\overleftarrow{Q}$ yields an equation suitable for the experimental determination of $\overleftarrow{Q}$:

$$\overleftarrow{Q} = Q[\mathbf{S_o}]_{tot,pss} / [\mathbf{S}]_{tot} \quad \text{(S32)}$$

According to equation (S25) $\vec{Q}$ is obtained as

$$\vec{Q} = Q - \overleftarrow{Q} \quad \text{(S33)}$$

In **Figure S3,** we show three fit versions assuming different values of $K \equiv K_{o,1} = K_{o,2}$ equal to 0.06, 0.08, 0.1. In each fit, the value of ϕ_{S_o} is fixed to a value of 0.0037, such that the $\vec{Q}$ value in solution without acid is exactly reproduced. The two other quantum yields $\phi_{\mathrm{S}_o\mathrm{H}^+}$, and $\phi_{\mathbf{S_o}\mathrm{H}_2^+}$ were left as free fitting parameters.

For K = 0.06, the fit curve clearly rises too early when passing pH$_{\text{non-aq}}$ = 0 to the negative direction. This is due to the fact that the contribution of $\mathbf{S_o}\text{H}^+$must compensate for the late rise of the contribution of $\mathbf{S_o}\text{H}_2^{2+}$

Table S1 Data used to fit the individual quantum yields for the ring-closing isomerization of the protolytic forms of $\mathbf{S_o}$ induced by irradiation with 313 nm light.[a]

equiv TFAH n × $[\mathbf{S}]_{\text{tot}}$	Q_{313} × 10^6	A$_{583}$ at PSS	%open in PSS	$\vec{Q}_{313}$ × 10^6	pH$_{\text{non-aq}}$ [b]	X$_o$ [c]	Y$_o$ [c]	Z$_o$ [c]
0	0.457	0.129	0.46	0.209	3.03	0.999	0.000	0.000
1	0.54	0.127	0.45	0.244	-0.32	0.719	0.240	0.040
5	1.14	0.232	0.82	0.940	-0.75	0.433	0.390	0.176
10	1.86	0.257	0.91	1.698	-0.95	0.290	0.414	0.295
20	3.32	0.267	0.95	3.150	-1.16	0.167	0.386	0.447
30	3.61	0.271	0.96	3.476	-1.30	0.108	0.345	0.548
50	3.75	0.273	0.97	3.638	-1.48	0.057	0.276	0.667
70	4.06	0.273	0.97	3.938	-1.60	0.036	0.230	0.734
140	5.63	0.273	0.97	5.461	-1.88	0.012	0.140	0.849

[a] Here, all calculations were carried out assuming $K_{o,1} = K_{o,2}$ = 0.08. [b]Calculated on the basis of equations (S1)-(S5) and equation (S11). [c]Theoretical coefficients calculated according to equations (S6) – (S10). To fit the pH$_{\text{non-aq}}$ –dependence of $\vec{Q}_{313}$ according to equation (S26), the following absorbances of the individual protolytic species of $\mathbf{S_o}$ were used: A_{S_o} = 0.706, $A_{\text{S}_\text{o}\text{H}^+}$ = 0.704, and $A_{\text{S}_\text{o}\text{H}_2^{2+}}$ = 0.687.

which is due to an obviously too low basicity of $\mathbf{S_o}\text{H}^+$ for the K value chosen. However, then $\mathbf{S_o}\text{H}^+$ already contributes too much in the overlapping region of $\mathbf{S_o}$ and $\mathbf{S_o}\text{H}^+$.

On the other hand, for K = 0.10, a negative quantum yield must be assumed for $\mathbf{S_o}\text{H}^+$to compensate the too early rising of the contribution of $\text{S}_\text{o}\text{H}_2^{2+}$ appearing as a consequence of an obviously somewhat to high basicity of $\mathbf{S_o}$ and $\mathbf{S_o}\text{H}^+$.

The value of K = 0.08 lies just in between the two latter cases and thus provides the best fit. Actually, here too, the quantum yield for $\mathbf{S_o}\text{H}^+$ is slightly negative, if complete freedom is admitted for the fit of $\phi_{\text{S}_o\text{H}^+}$, and $\phi_{\mathbf{S_o}\text{H}_2^+}$. It is demonstrated in **Figure S3**, that setting $\phi_{\text{S}_o\text{H}^+}$ to zero would not significantly affect the qualitiy of the fit, and that the upper limit of $\phi_{\text{S}_o\text{H}^+}$, set by the experimental accuracy, would be clearly below a value of 0.01.

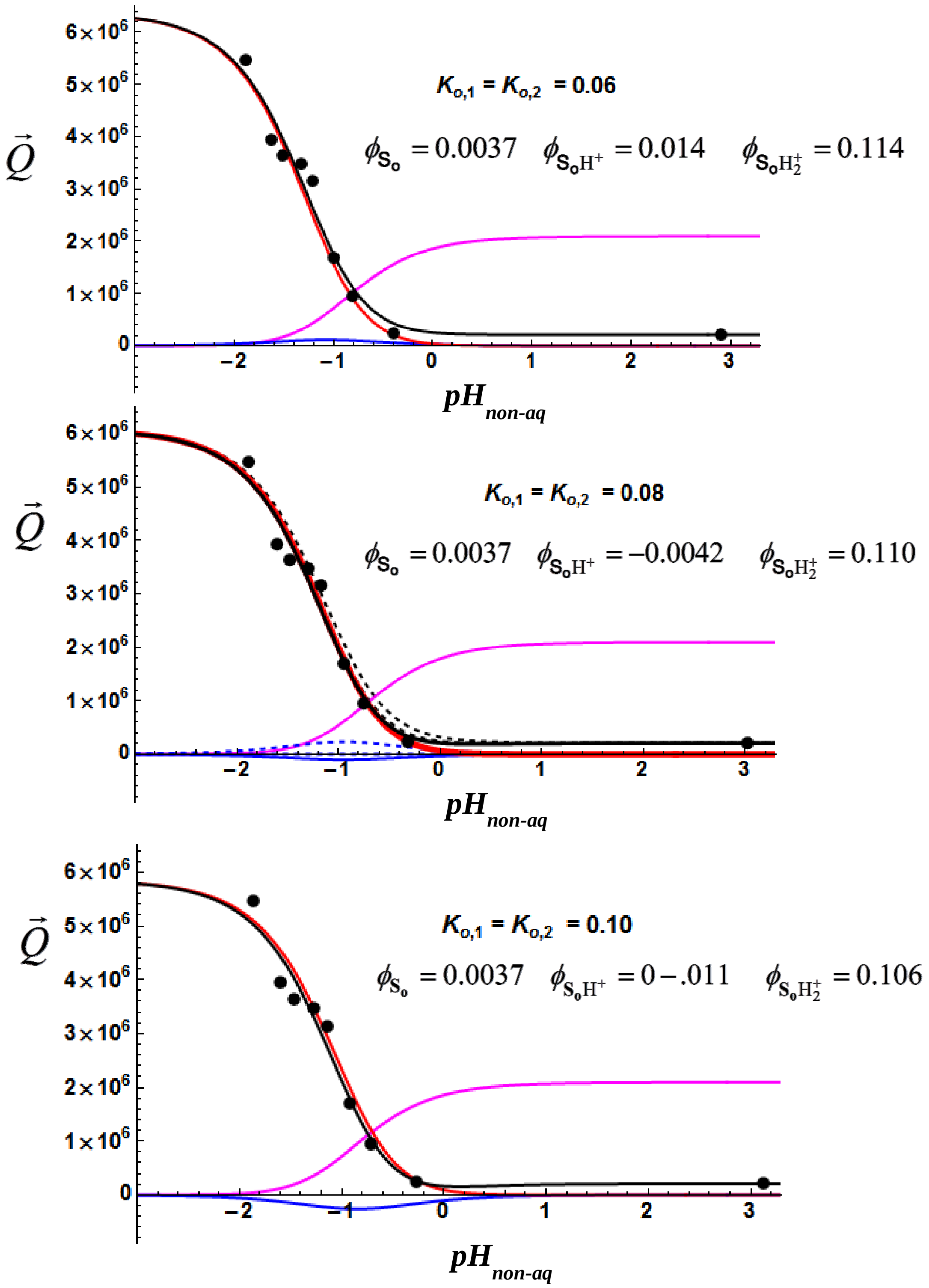

Figure S3 Fits of the pH$_{\text{non-aq}}$ dependence of the observed partial pseudo quantum yield $\vec{Q}$ (black data points), calculated for three cases of $K_{o,1} = K_{o,2}$ values. Black lines: total simulated value of $\vec{Q}$, magenta lines: contributions of $\mathbf{S_o}$, scaled by a factor of 10 for better visibility, blue lines: contributions of $\mathbf{S}_o\mathrm{H}^+$, red lines: contributions of $\mathbf{S}_o\mathrm{H}_2^{2+}$. The fits were forced to reproduce the data point in non-acidified solution exactly, thereby fixing the quantum yield for $\mathbf{S_o}$ to $\phi_{S_o} = 0.0037$. The other quantum yields were obtained from a free least squares fit using *Mathematica*. In case of $K_{o1} = K_{o,2} = 0.08$, the effect of a quantum yield adaptation for $\mathbf{S}_\mathrm{o}\mathrm{H}^+$ is also shown: $\phi_{\mathbf{S}_\mathrm{o}\mathrm{H}^+} = -0.0042$ (free fit, solid blue line for contribution of $\mathbf{S}_\mathbf{o}\mathrm{H}^+$ to $\vec{Q}$, solid black line for total value of $\vec{Q}$), $\phi_{\mathrm{S}_o\mathrm{H}^+} = 0.0$ (set value, broken blue horizontal line for contribution of $\mathbf{S}_\mathbf{o}\mathrm{H}^+$ to $\vec{Q}$, lower broken black line for total value of $\vec{Q}$), $\phi_{\mathrm{S}_o\mathrm{H}^+} = 0.01$ (set value, upper broken blue line for contribution of $\mathbf{S}_\mathbf{o}\mathrm{H}^+$ to $\vec{Q}$, upper broken black line for total value of $\vec{Q}$).

The fit of the ring-opening photokinetics for irradiation at 313 nm is shown in **Figure S4.**

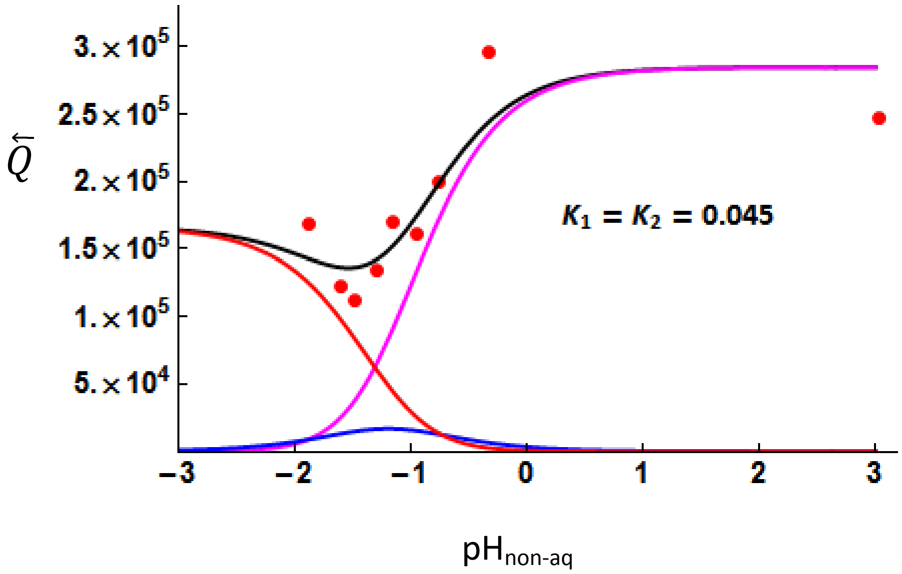

Figure S4 Partitioning of pseudo quantum yield $\overleftarrow{Q}$ for the ring-opening isomerization at 313 nm into contributions of individual protolytic forms of $\mathbf{S_c}$ (magenta), $\mathbf{S}_\mathrm{c}\mathrm{H}^+$ (blue) and $\mathbf{S}_\mathrm{c}\mathrm{H}_2^{2+}$ (red) of the closed form as a function of $\mathrm{pH}_{\text{non-aq}}$. Red dots represent measured data points. The black curve represents the best fit of the dataset with the following parameters: $A_{\mathbf{S_c}} = 0.507$, $A_{\mathbf{S_c}\mathrm{H}^+} = 0.543$, $A_{\mathbf{S_c}\mathrm{H}_2^+} = 0.570$, $\phi_{\mathbf{S_c}} = 0.007$, $\phi_{\mathbf{S_c}\mathrm{H}^+} = 0.001$, $\phi_{\mathbf{S_c}\mathrm{H}_2^+} = 0.004$. Error margins of quantum yields ±30%.

References:

S1) Hammett, L. P.; Deyrup, A. J., *J. Am. Chem. Soc.* **1932**, *54*, 2721-2739.

S2) Hammett, L. P., *Physical organic chemistry: reaction rates, equilibria, and mechanisms*. McGraw-Hill Book Company, 1940.