

Electronic Supplementary Information

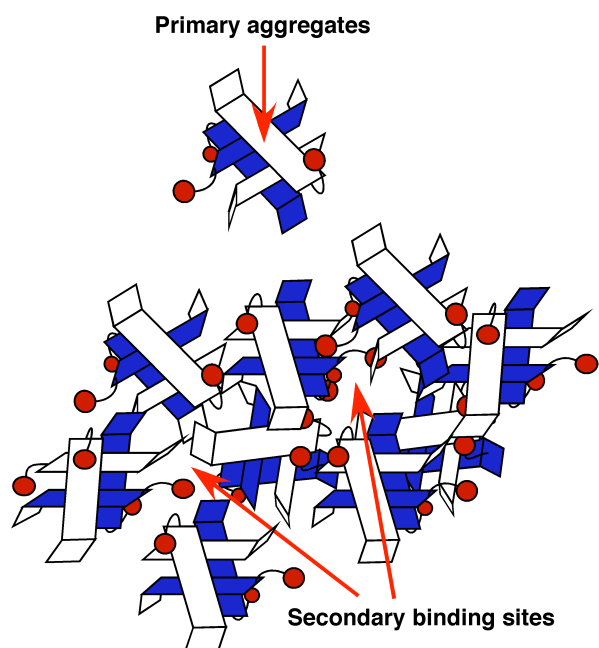
Aqueous Solubilization of Photochromic Compounds by Bile Salt Aggregates

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Scheme S1. Cartoon representation for bile salt aggregates in water. Areas shaded in blue correspond to the hydrophobic face of the bile salt monomer, areas in white correspond to the faces with hydroxyl groups and the red circles are the charged head groups. At low bile salt concentration small primary aggregates are formed while these continue aggregating as the bile salt concentration is raised. The solubilization of **1** and **2** can occur in either primary or secondary aggregates and their location was not determined.

Experimental section. *Materials.* Sodium chloride, (NaCl, ACP, $\geq 99.0\%$), sodium cholate, (NaC, Aldrich, 98%), 1',3',3'-trimethyl-6-nitrospiro[2H-1]-benzopyran-2,2'-indoline, (**1**, TCI), 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene), (**2**, TCI), ethyl alcohol (95%), and acetonitrile (EMD, HPLC grade, $\geq 99.8\%$) were used

as received. Deionization water ($\geq 17.8 \text{ M } \Omega \text{ cm}^{-1}$, Sybron Barnstead system) was employed for sample preparation.

Hg-arc or Xe-arc lamps were employed for irradiation and the excitation wavelength was selected with a monochromator. Absorption spectra were collected with a Varian Cary 1 spectrometer at room temperature. Kinetic measurements were performed at a single wavelength on a Varian Cary 5 spectrometer at constant temperature ($25 \text{ }^\circ\text{C}$), using a multiple sample holder. A control cell containing all chemicals with the exception of **1** sat in the light beam and at regular intervals the sample cell was moved into the beam to measure its absorbance. This procedure is required to avoid the photochemical bleaching of **1b**. The absorbance for the control cell was subtracted from the values measured for the sample in order to account for any baseline drift.

Bile salts were dissolved in aqueous NaCl solutions (0.20 M or 1.0 M). Photochromic compounds were dissolved in acetonitrile (1 mM). A desired volume of this stock solution was injected into the bile salt aqueous solution or ethanol. The final concentrations were 30 – 200 μM for **1** and 20 – 300 μM for **2**.

All solutions containing bile salt, with the exception of the solubilization experiments, were shaken or left standing overnight, and were then heated at $50 \text{ }^\circ\text{C}$ for 30 min and cooled down to room temperature to break up any bile salt gel formed.¹ For the solubilization experiments, the bile salt aqueous solutions were heated at $50 \text{ }^\circ\text{C}$ for 30 min and cooled down to room temperature before injection of the stock solution of the photochromic compounds. The samples were not stirred or heated after this injection. The absorbance spectra were collected at least 1 h after the sample preparation and were collected again after 24 h. After the latter measurement the solutions were heated at $50 \text{ }^\circ\text{C}$ for 30 min, cooled to room temperature and the spectra were again collected.

For the relative coloration experiments, the concentrations of **1a** and **2a** in the bile salts and ethanol were adjusted to a constant absorbance at the irradiation wavelength ($A_{340} = 0.32 \pm 0.02$ for **1a** and $A_{272} = 0.60 \pm 0.02$ for **2a**). Before starting the coloration experiments the samples were left on the bench exposed to ambient light, which was sufficient to convert any **1b** to **1a** as confirmed by the solution's absorption spectrum. For the coloration experiment the light intensity was adjusted by varying the slit of the monochromator to ensure a low conversion, which led to a linear relationship between the formation of **1b** or **2b** and the irradiation time (reaction under zero order condition). The sample of **1a** was irradiated at 340 nm, while the solution of **2a** was irradiated at 272 nm. Periodically the sample was removed from the irradiation set-up and its absorbance was measured in the visible region where **1b** and **2b** absorb. This work was performed in the dark to eliminate any photochemical switching due to the laboratory lighting.

For the relative decoloration experiments of **2**, the concentrations of **2b** in the bile salt solutions and in ethanol were adjusted by irradiating the samples at 272 nm to achieve a constant absorbance at 577 nm ($A_{577} = 0.254 - 0.255$). The decoloration experiments were performed by irradiating the samples at 577 nm and periodically measuring the absorbance of the solutions at 577 nm. This work was also performed in the dark.

The thermal coloration/decoloration rate constants of **1** were determined recording the absorbance at 517 nm for at least 24 h at 25 °C after obtaining predominantly each isomer. Compound **1b** was obtained by irradiating the samples at 338 nm for 30 – 60 min. The absorbance measurement started after a time interval of 3 to 40 min. This waiting period did not affect the values for the rate constants obtained. Solutions with predominantly **1a** were obtained by exposing the samples to ambient light for at least 15 min. The decays were fit to a sum of two exponentials (equation 1 in manuscript) using the fitting routine in Kaleidagraph.

Photochemical switching of aqueous solutions of 2 in the presence of NaC. Irradiation of **2a** in the presence of different concentrations of bile salt led to the formation of **2b** and the absorption maxima for **2b** were the same at all bile salt concentrations investigated.

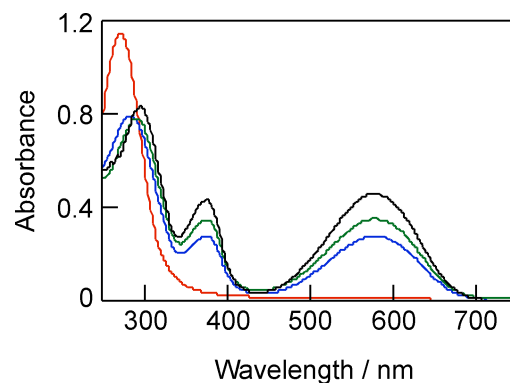


Figure S1. Absorption spectra for aqueous solutions (0.20 M NaCl) of **2** before irradiation (red) and after irradiation at 272 nm in the presence of 20 mM NaC (blue), 40 mM NaC (green) and 80 mM NaC (black). The photon flux for each experiment was different and the magnitude of the absorption for **2b** is not a measure on the coloration efficiency.

Photocycling between isomers of 1 and 2. Irradiations were performed with a wide bandwidth for slits on the monochromator (36 nm) to ensure the fastest possible conversion between the isomers. In the case of compound **1** in the presence of 80 mM NaC and 0.20 M NaCl, the sample was irradiated at 340 nm for 10 min and followed by an irradiation at 513 nm for 10 min, up to 20 cycles (Fig. S2). In the case of compound **2** in the presence of 80 mM NaC and 0.20 M NaCl, the sample was irradiated at 272 nm for 10 min and followed by irradiation at 577 nm for 140 min, up to 10 cycles (Fig. S3). The spectra for **2** were the same after cycling between isomers and the variability in the absorbance measurements is due to incomplete switching. In the case of **1**, thermal decomposition may have occurred (see Fig. S9 below), leading to the continuous decrease in the absorption of **1b** during cycling.

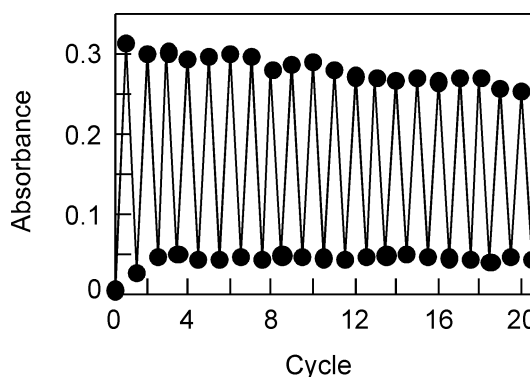


Figure S2. Cycling for the absorbance at 513 nm between **1a** and **1b** by irradiating the samples at 340 nm followed by irradiation at 513 nm.

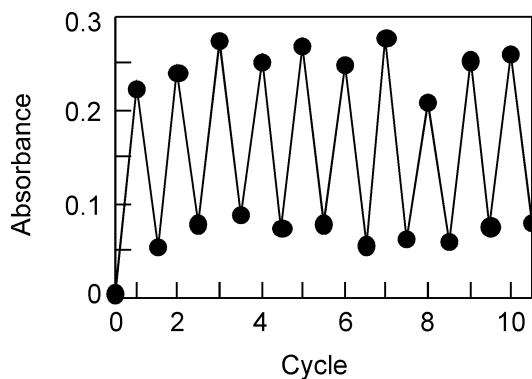


Figure S3. Cycling for the absorbance at 577 nm between **2a** and **2b** by irradiating the samples at 272 nm followed by irradiation at 577 nm.

Solubilization experiments.

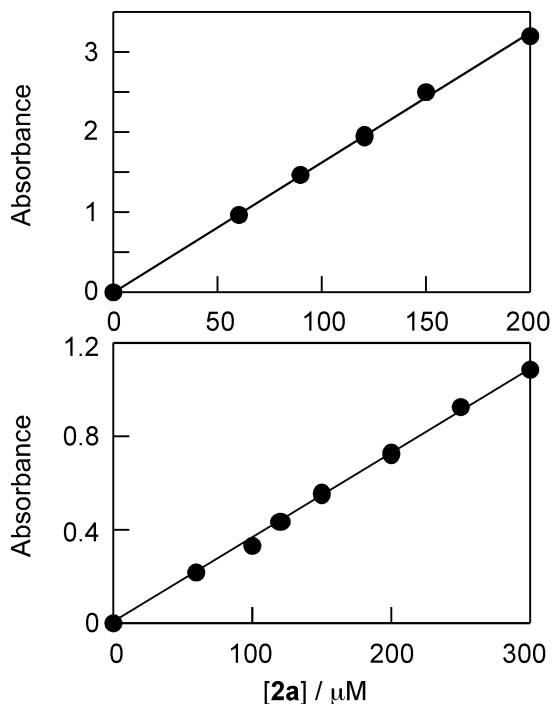


Figure S4. Dependence in the presence of 80 mM NaC and 0.20 M NaCl of the absorption of **2a** with its concentration measured at 272 nm (top) and 310 nm (bottom). Higher concentrations of **2** cannot be measured at 272 nm because the spectrometer reaches saturation.

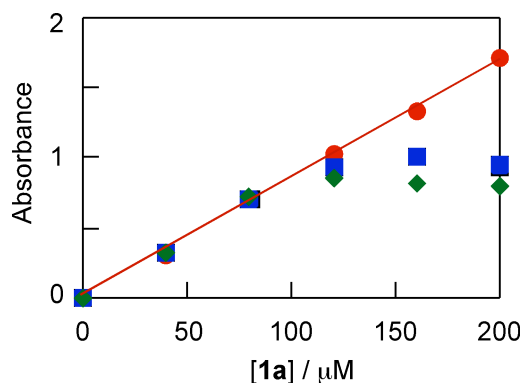


Figure S5. Dependence in the presence of 80 mM NaC and 0.20 M NaCl of the absorption of **1a** with its concentration measured at 338 nm for freshly prepared solutions (circles, red), after 24 h (squares, blue) and after 24 h and a 30 min heating cycle (diamonds, green).

Relative colorability studies.

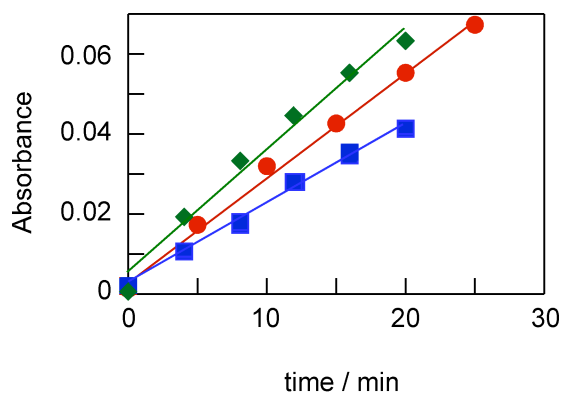


Figure S6. Changes in the absorption for the formation of **1b** when a solution of **1a** was irradiated at 340 nm in ethanol (533 nm, diamonds, green), in the presence of 80 mM NaC/ 0.20 M NaCl (513 nm, circles, red) and 40 mM NaC/0.20 M NaCl (508 nm, squares, blue).

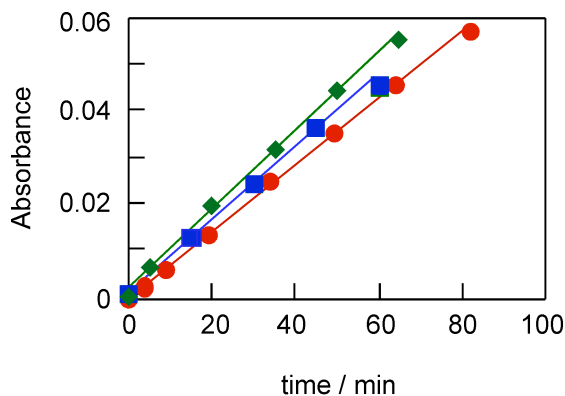


Figure S7. Changes in the absorption at **2b** when solutions of **2a** were irradiated at 272 nm in ethanol (567 nm, diamonds, green), in the presence of 80 mM NaC/ 0.20 M NaCl (577 nm, circles, red) and 40 mM NaC/0.20 M NaCl (577 nm, squares, blue).

Relative decoloration studies.

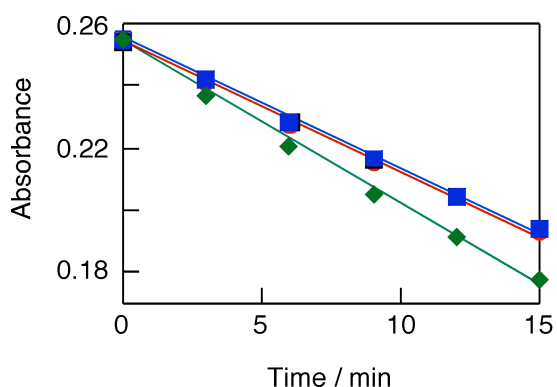


Figure S8. Changes in the absorption at **2b** at 577 nm when solutions of **2b** were irradiated at 577 nm in ethanol (diamonds, green), in the presence of 80 mM NaC/0.20 M NaCl (circles, red) and 40 mM NaC/0.20 M NaCl (squares, blue).

Thermal decomposition of 1. Aqueous bile salt solutions of **1** slowly decompose over time. This decomposition was assigned to the hydrolysis of **1**.² The decomposition leads to the appearance of a shoulder around 400 nm. The decomposition is sped up with heat and it was slowed when a higher concentration of NaCl was employed in the presence of NaC. The latter observation is consistent with the lower k_2 values measured in the presence of 1.0 M NaCl when compared to the kinetics measured for bile salt solutions containing 0.20 M NaCl. This trend is observed for the kinetics when either **1a** or **1b** are formed in excess (Table 1 in manuscript).

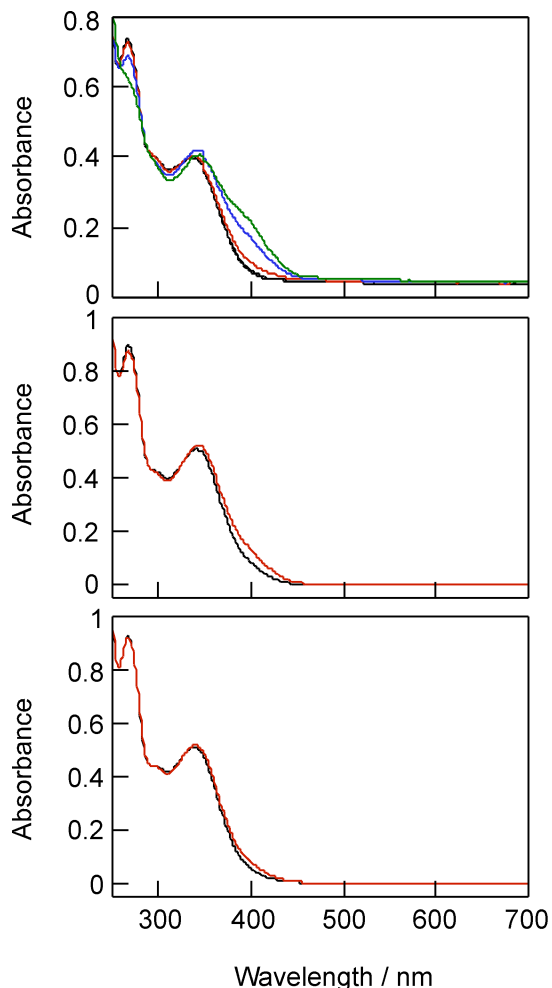


Figure S9. Changes in the absorption of **1** over time. *Top:* 40 μM of **1** in the presence of 80 mM NaC and 0.20 M NaCl for a freshly prepared solution and after 24 h (the spectra were the same) (black), after 24 h and heating (red), after 8 days in the dark (blue) and after 12 days (green). *Middle and bottom:* 50 μM of **1** in the presence of 80 mM NaC and 0.20 M NaCl (*middle*) or 1.0 M NaCl (*bottom*) after sample preparation (black) and after 29 h (red). Both samples were left for 15 min on the bench to convert any remaining **1b** to **1a** before the absorption spectra were measured.

References

1. Y. Li, J. F. Holzwarth and C. Bohne, *Langmuir*, 2000, 16, 2038-2041.
2. T. Stafforst and D. Hilvert, *Chem. Commun.*, 2009, 287-288.