Electronic Supplementary Information

Excited-State Acidity of the 8-Hydroxyacridizinium Ion - A Water-Soluble Photoacid

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Materials and methods

The 8-hydroxyacridizinium bromide **1a** and the 8-methoxyacridizinium bromide **1b** were prepared according to literature procedures.[1] Solvents employed in spectroscopic experiments were of spectral grade; deionized water (resistivity: $\rho \geq 18\ \mathrm{M\Omega\,cm^{-1}}$) was used for the preparation of the buffer solutions.

Spectrophotometric measurements.

Absorption spectra were recorded on a Varian Cary 100 double-beam spectrophotometer; steady-state fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. All spectrophotometric measurements were performed in thermostated quartz sample cells at 20 °C, using spectral grade solvents (Fluka, Riedel-de Haën). The solution concentrations were 1×10^{-4} M for absorption spectroscopy and 1×10^{-5} M for fluorescence spectroscopy. Spectrophotometer slit widths were set to bandwidths of 5 nm for emission spectroscopy. The relative fluorescence quantum yields were determined by the standard method[2] with Coumarin I (laser grade, Acros Organics, ϕ_{fl} = 0.73 in ethanol) as a reference.

Spectrophotometric pH titrations

To a solution of **1a** ($c = 1.0 \times 10^{-4}$ M) in Britton-Robinson buffer[3] (4.0 mM H_3PO_4, 4.0 mM H_3BO_3, 4.0 mM NaOAc, adjusted to pH 7 by addition of aq. NaOH) were added aliquots of aq. HCl (2 M) or aq. NaOH (2 M). After each titration step, the pH and the absorption spectra were determined. The titration was performed in the pH range between 1 and 10, and the data from UV spectra were plotted as

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[1] C. K. Bradsher and J. H. Jones, J. Am. Chem. Soc. 1957, 79, 6033-6034.

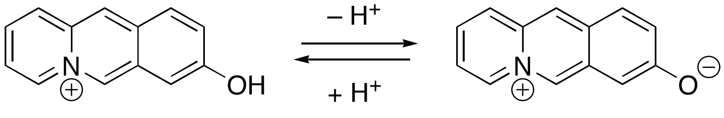
[2] a) J. N. Demas and G. A. Crosby, J. Phys. Chem. 1971, **75**, 991–1024; b) B. Valeur, *Molecular Fluorescence*, Wiley-VCH Verlag GmbH, Weinheim, 2002.

[3] H. T. S. Britton and R. A. Robinson, J. Chem. Soc. 1931, 458-473.

a function of pH of the solution. To obtain the value of the acidity constant, the titration isotherms were numerically fitted to the Henderson-Hasselbalch equation (Eq.1, Figure S1).[4]

$$A = \frac{A_{\mathrm{HA}}\,10^{-\mathrm{pH}} + A_{\mathrm{A}}\,10^{-\mathrm{p}K\mathrm{a}}}{10^{-\mathrm{pH}} + 10^{-\mathrm{p}K\mathrm{a}}} \qquad \text{(Eq.1)}$$

A: absorbance at the fixed monitor wavelength (378 nm) in the course of titration; A_{HA}: absorbance of **1a** at the fixed wavelength; A_{A}: absorbance of the **1a$^{\mathbf{cB}}$** at the fixed wavelength (see Scheme S1 for structures of **1a** and **1a$^{\mathbf{cB}}$**).



1a **1a$^{\mathbf{cB}}$**

Scheme S1.

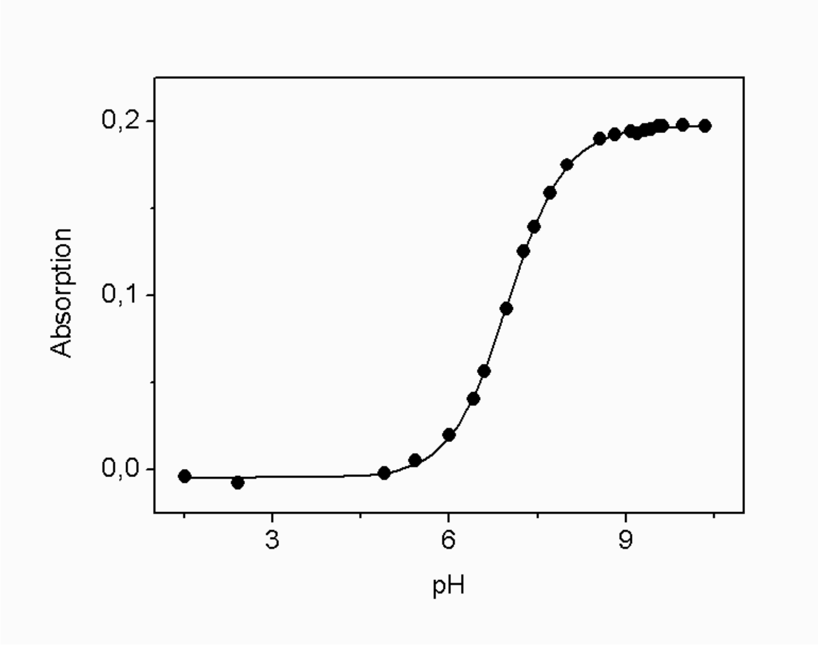


Figure S1. Plot of pH-value *versus* absorption intensity of **1a** at $\lambda = 460$ nm ($c = 10^{-4}$ M); straight line: fit of the data to Eq. 1.

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[4] J. Polster and H. Lachmann, *Spectrometric Titrations: Analysis of Chemical Equilibria*, VCH, Weinheim, 1989.

Spectrofluorimetric titrations

Emission spectra (λ_{ex} = 395 nm) of **1a** were recorded in perchloric acid solutions at concentrations ranging from 11.7 to 0.1 M and in aq. NaOH solutions at concentrations ranging from 0.1 to 0.01 M. The excited-state acidity constant p*K*a* was estimated according to the Förster cycle (Eq. 2).

$$\Delta pK = 0.00209\,[\tilde{\nu}(A) - \tilde{\nu}(HA)]/cm^{-1} \qquad (\text{Eq. 2})$$

$\tilde{\nu}$ (A) = 0-0 transition of the deprotonated **1a^{cB}**, in wavenumbers

$\tilde{\nu}$ (HA) = 0-0 transition of the deprotonated **1a**, in wavenumbers

The 0-0 transitions were obtained from from the point of intersection between the normalized long-wavelength absorption and emission bands of **1a** and **1a^{cB}** (Figure S2)

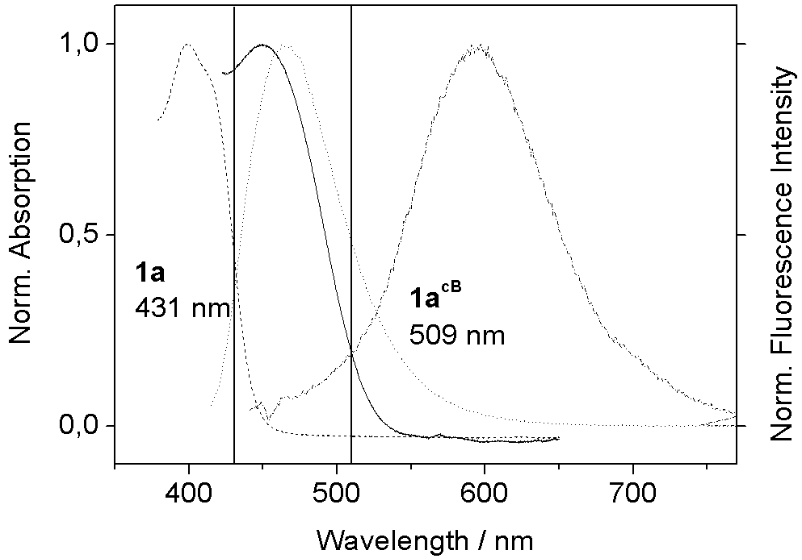

Figure S2. Normalised absorption and emission spectra of **1a** and **1a^{cB}** that were employed to estimate the 0-0 transition (vertical lines).

Correlation of absorption maxima with selected solvent parameters

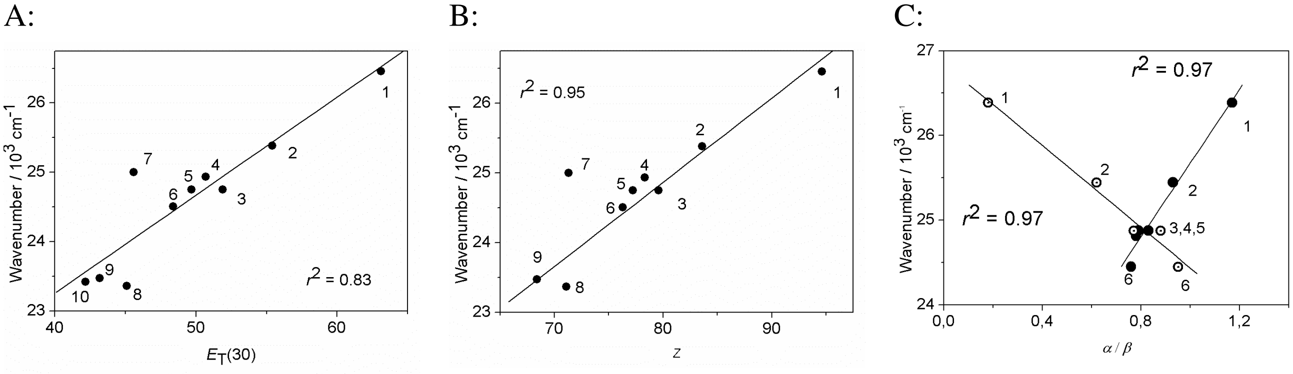

Figure S3. Correlation of the absorption maxima (in cm^{-1}) of **1a** ($c = 10^{-4}$ M) in different solvents (1: water, 2: MeOH, 3: EtOH, 4: 1-PrOH, 5: 2-PrOH, 6: 1-BuOH, 7: CH_3CN, 8: DMSO, 9: DMF, 10: NMP) with the solvent parameters $E_T(30)$ (A), Z (B), α, and β (C; ●: α, ❍: β).

Emission spectra of 1a in different solvents

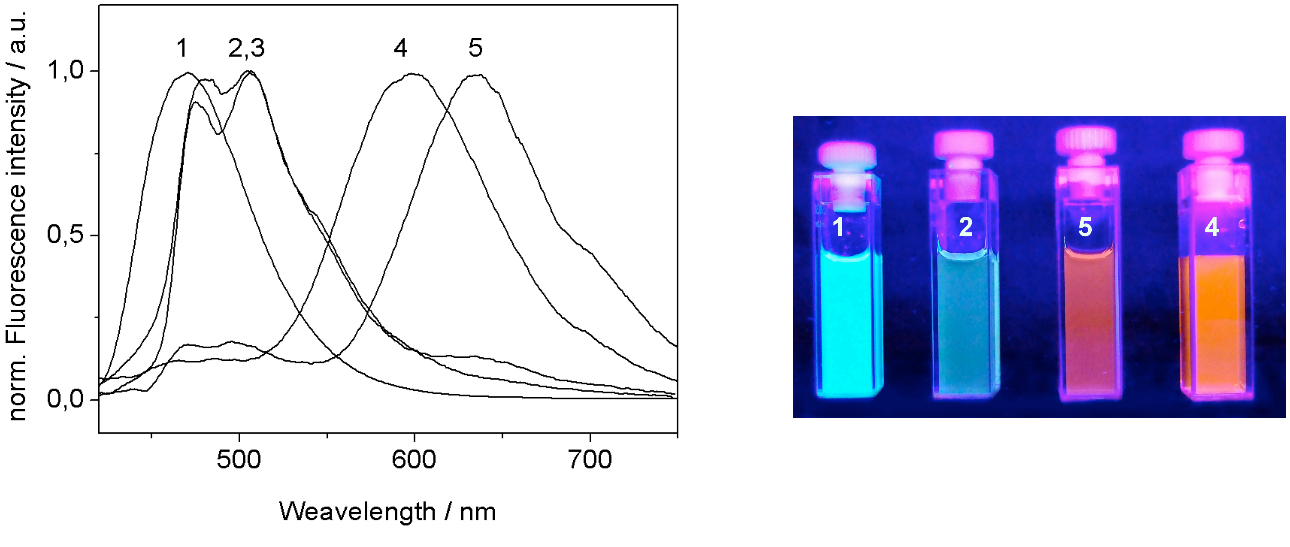

Figure S4. Left: Normalized fluorescence emission spectra of **1a** ($c = 10^{-5}$ M) in different solvents (1: MeCN, 2: DMSO, 3: DMF, 4: H_2O, 5: EtOH); $\lambda_{ex} = 395$ nm. Right: Picture of fluorescence of **1a** ($c = 10^{-4}$ M) in different solvents (1: MeCN, 2: DMSO, 4: H_2O, 5: EtOH); $\lambda_{ex} = 366$ nm.