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pH-Dependent molecular switch based on P^V porphyrin

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Materials and Methods

Pyridine, $POBr_3$, MeOH, CH_2Cl_2, *n*-C_6H_{14}, $CHCl_3$, and *p*-aminophenol were available from commercial suppliers. Alumina for column chromatography was purchased from Merck. Chloroform (stabilized with 0.6−1% ethanol) was dried over $CaCl_2$ and distilled over CaH_2.

Spectroscopic studies

NMR spectra were recorded on a Bruker Avance 600 spectrometer. ^1H NMR spectra were referenced to the residual solvent signal. UV−Vis spectra were measured with a Thermo Evolution 210 spectrophotometer in quartz cells with a 1 cm optical path. Matrix-assisted laser desorption ionization time-of-flight mass spectra were measured on a Bruker Daltonics Ultraflex spectrometer. High-resolution mass spectra (HRMS) were recorded on an Orbitrap electrospray ionization time-of-flight (ESI-TOF) mass spectrometer. ^1H, ^{31}P, ^1H-^{15}N HMBC NMR spectra were recorded at 25 °C using Bruker Avance NMR spectrometers: AV300 (300 MHz) and AV600 (600 MHz).

Fluorescence quantum yields

Fluorescence spectra (Φ_F, λ_{ex}= 425 нм) were recorded at room temperature using a Horiba Scientific Fluorolog fluorimeter. Fluorescence quantum yields (Φ_F) were determined by the comparative method:

$$\Phi_F = \Phi_{st} \frac{F\, A_{st}\, n^2}{F_{st}\, A\, n_{st}^2}$$

where F, F_{st} – are the areas under the fluorescence emission curves of the samples and the standard, respectively; A, A_{st} –are the respective absorbances of the samples and standard at the excitation wavelengths, respectively; n, n_{st} – refractive indices of solvents for the substance and standard respectively.

Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ, λ_{ex} = 532 нм) were determined in air in DMSO solutions using the relative method with unsubstituted H_2TPP as reference. Typically, a 2.5 mL portion of the respective porphyrin complex solutions (~10^{-6} M) containing the singlet oxygen trap was irradiated with a 532- nm light. DPBF was used as a chemical trap for singlet oxygen in DMSO. Equation (2) was employed for the calculations:

$$\Phi_\Delta = \Phi_{\Delta st} \frac{R \times \mathrm{I}_{st}}{\mathrm{R}_{st} \times I}$$

where $\Phi_{\Delta St}$ is the singlet oxygen quantum yield for the standard H_2TPP ($\Phi_{\Delta st}$=0.57 in DMSO), R and R_{St} are the DPBF photobleaching rates in the presence of the samples and standard, respectively. I and I_{St} are the rates of light absorption by the samples and standards, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen, the concentration of the trap was lowered to $5 \cdot 10^{-5}$ M.

Experimental procedures

Di(*p*-aminophenyloxy)-((5,10,15,20-tetraphenyl)porphyrinato)phosphorus(V) bromide, [(TPP)P(O-Ph-NH_2)$_2$]$^+$Br$^-$ (1a)

Free porphyrin base H_2TPP (**1**) (50 mg, 0.081 mmol, 1 eq.) was dissolved in pyridine (10 ml) under argon. To the resulting mixture a suspension of $POBr_3$ (0.55 g, 2.025 mmol, 25 eq.) in pyridine (10 ml) was added dropwise and was refluxed under argon for 30 min with stirring. Then a solution of *p*-aminophenol (0.707 g, 6.43 mmol, 80 eq.) in pyridine (10 ml) was added dropwise to the reaction mixture, and a precipitate was formed. The target complex **1a** was isolated by column chromatography on alumina (*n*-C_6H_{14}:CH_2Cl_2:MeOH (100:0:0 – 0:95:5 vol %)). The product was additionally purified by size-exclusion chromatography with BioBeads SX-1 in $CHCl_3$ + 2.5 vol % MeOH yielding 5 mg of a purple powder (9%).

^{1}H NMR ($CDCl_3$, 600 MHz) δ, ppm.: 1.97 (dd, *J* = 8.9, 2.8 Hz, 4H, *o*-aminophenyl), 5.28 (d, *J* = 8.5 Hz, 4H, *m*-aminophenyl), 7.70 -7.79 (m, 12H, *m*- and *p*- phenyl), 7.68 (d, *J* = 7.2 Hz, 8H *o*- phenyl), 8.98 (d, *J* = 3.0 Hz, 8H, β-pyrr).

^{13}C NMR ($CDCl_3$, 151 MHz) δ, ppm: 141.70, 141.36, 140.19, 135.52, 133.86, 133.37 (d, *J* = 5.4 Hz), 131.19, 130.41, 130.16, 129.11, 128.66, 117.47, 115.69 (d, *J* = 8.3 Hz), 114.78

^{31}P NMR ($CDCl_3$, 162 MHz) δ, ppm: -189.

UV–Vis [$CHCl_3$; λ_{max}, nm (A_{rel})]: 425 (1.00), 563 (0.04).

UV–Vis [H_2O; λ_{max}, nm (log ε, M^{-1} cm^{-1})]: 423 (4.31), 563 (3.18), 604 (2.85).

HR-ESI MS (m/z*)* Calculated for $C_{56}H_{40}N_6O_2P$ $[M]^+$: 859.2945. Found: 859.2947.

Results and Discussion

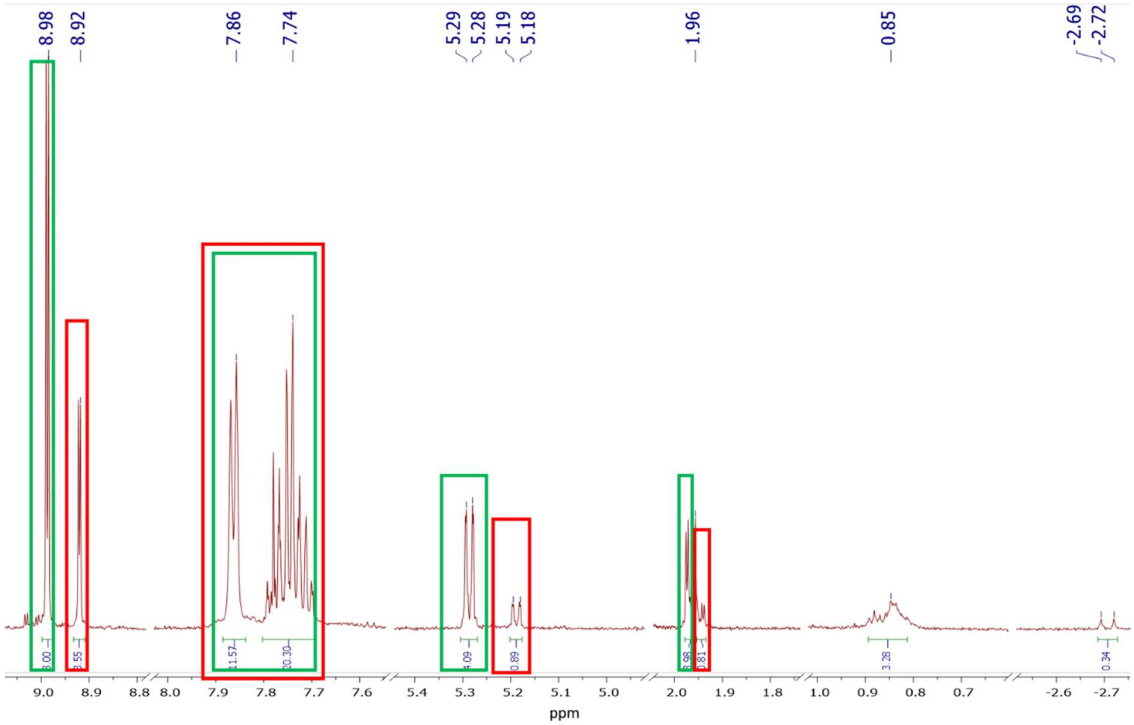

Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of reaction mixture after filtration through Al_2O_3 layer. The colors highlight signals of two isomers: **1a** (green) and **1b** (red)**.**

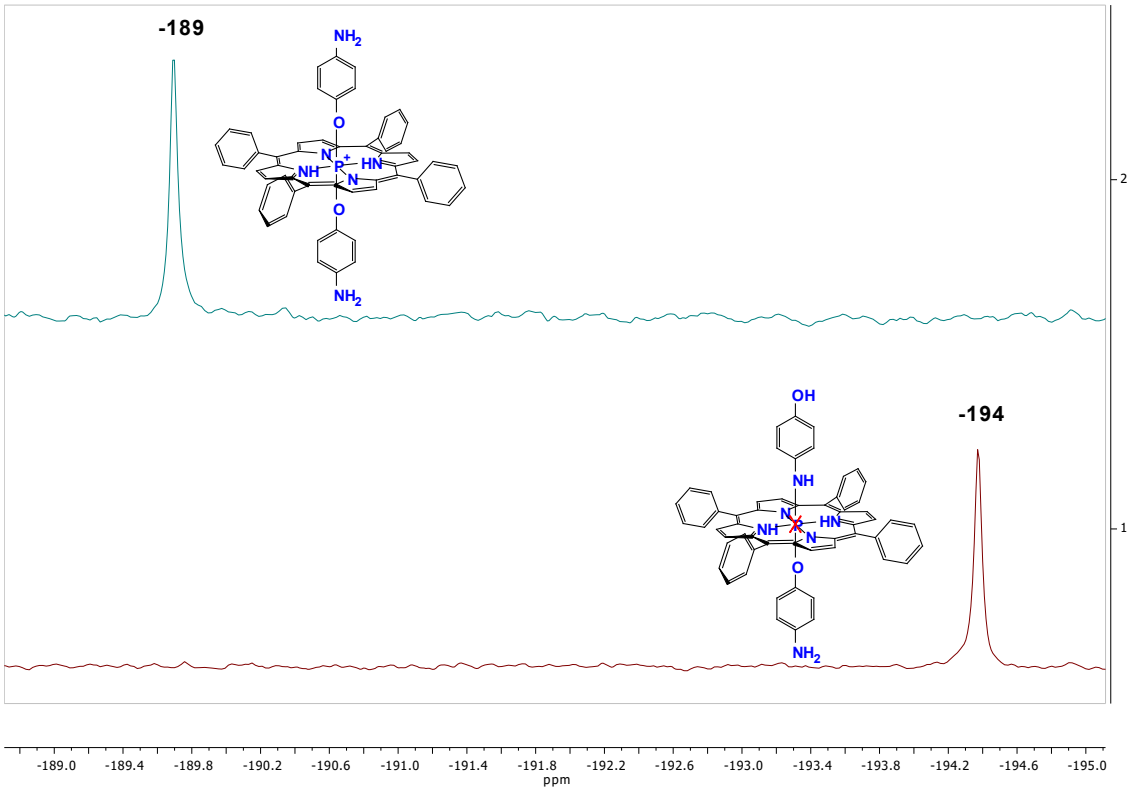

Figure S2. ^{31}P NMR spectrum ($CDCl_3$, 162 MHz) of **1a** (blue) and **1b** (red)**.**

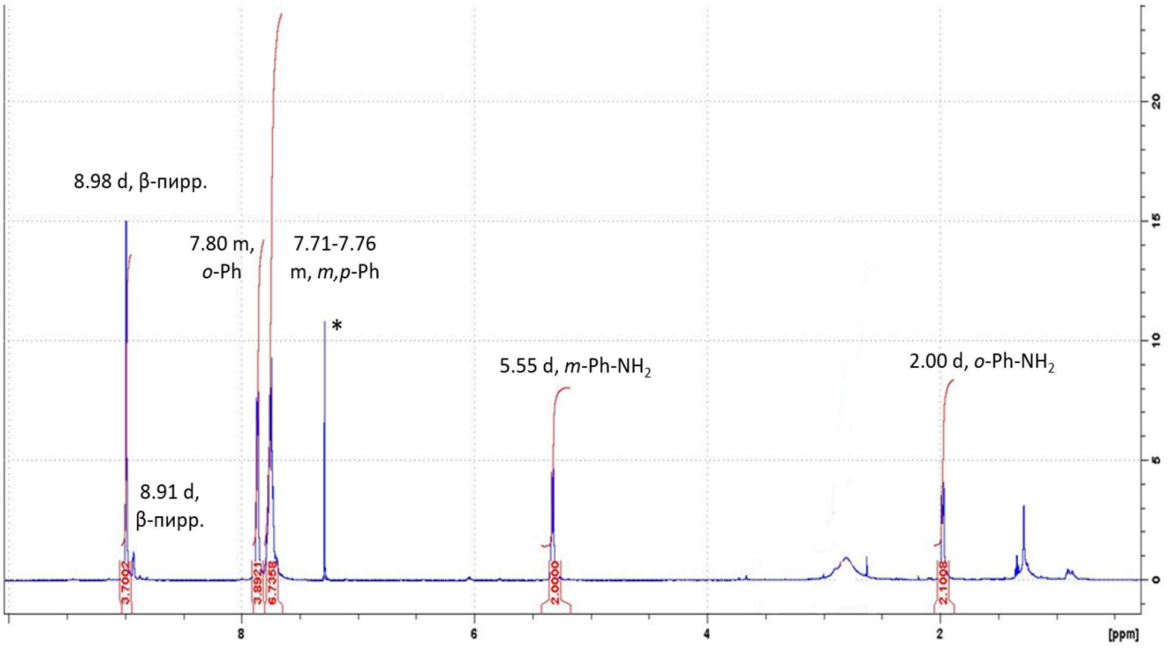

Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **1a**.

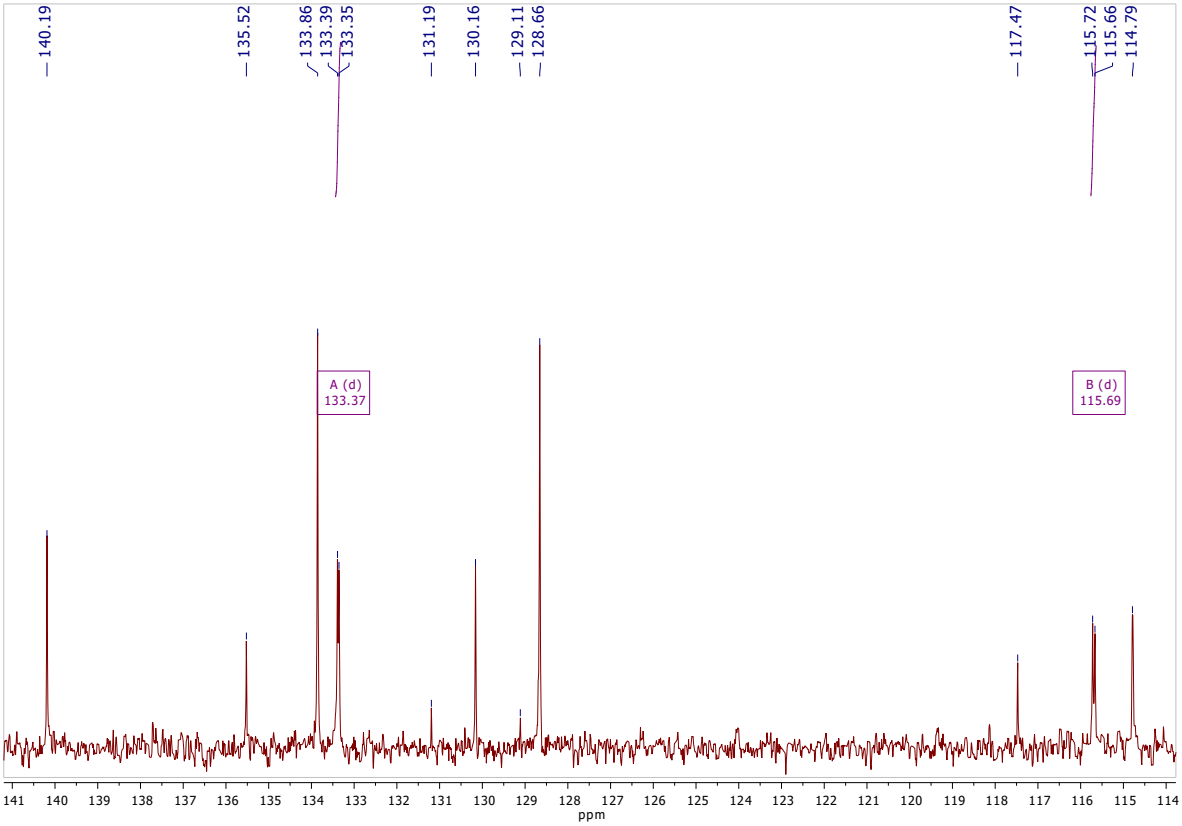

Figure S4. ^{13}C NMR ($CDCl_3$, 151 MHz) of **1a.**

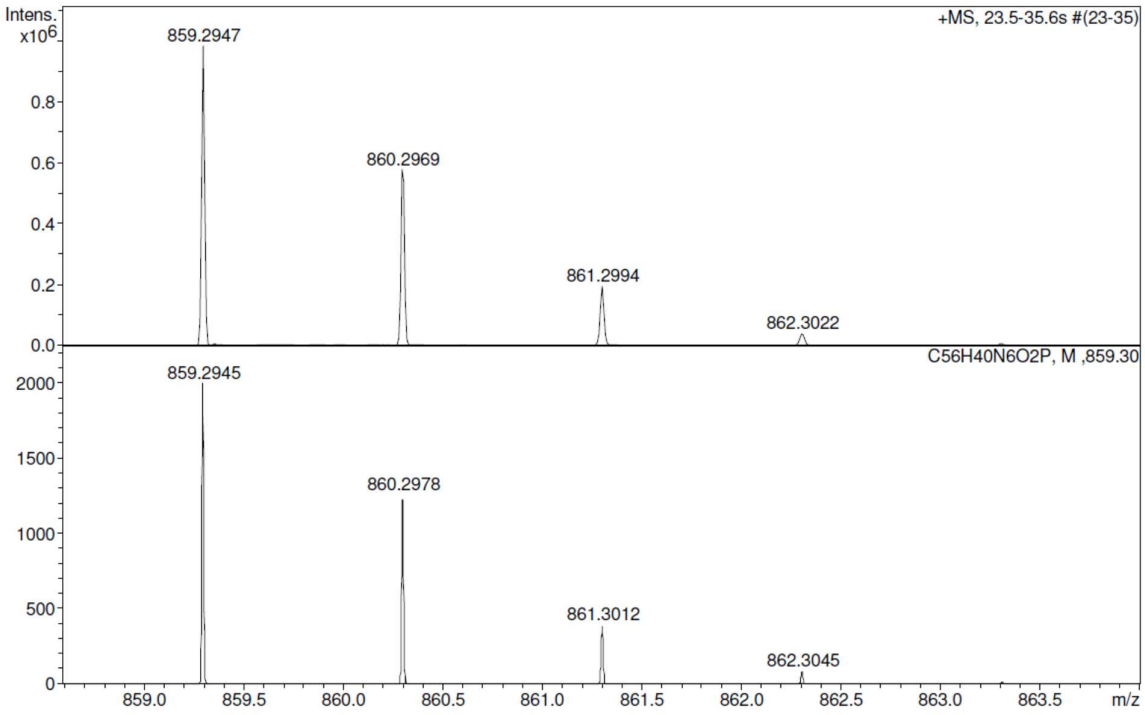

Figure S5. ESI HRMS spectra of **1a**: experimental *(top)*, calculated *(bottom)*.

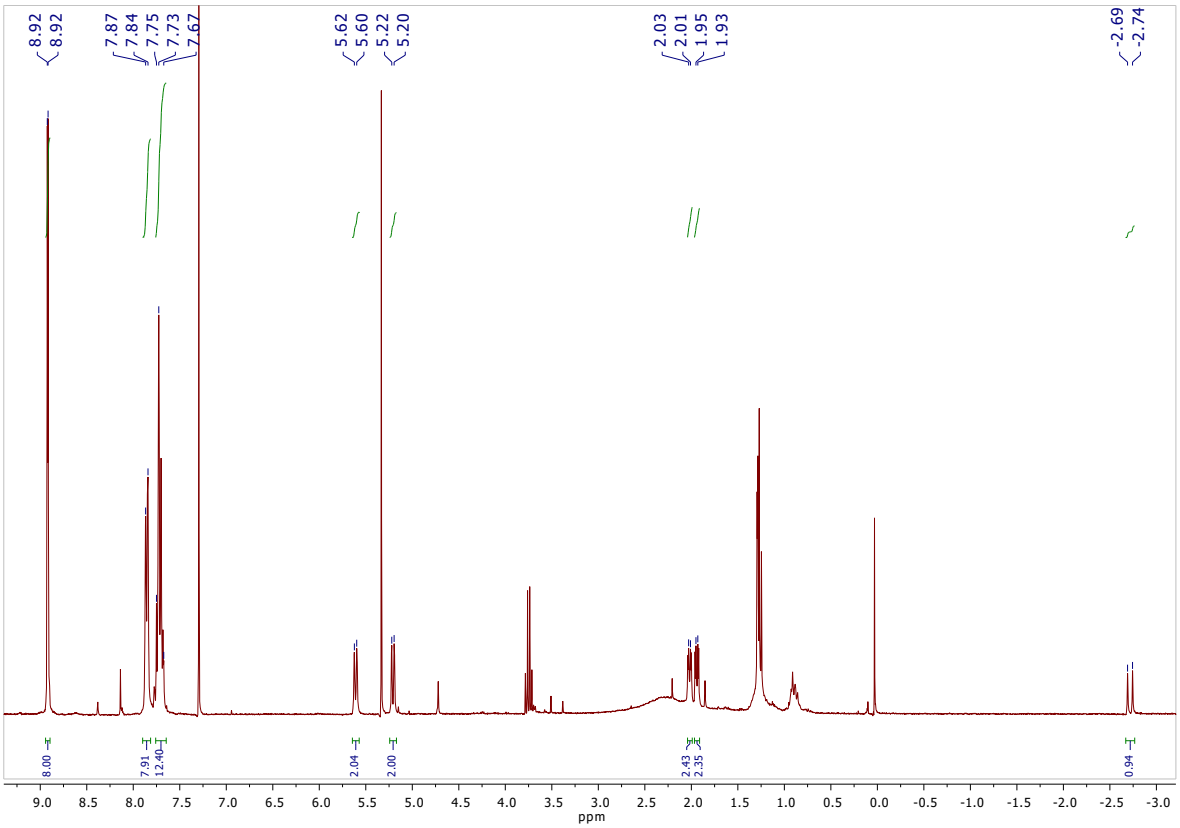

Figure S6. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **1b**.

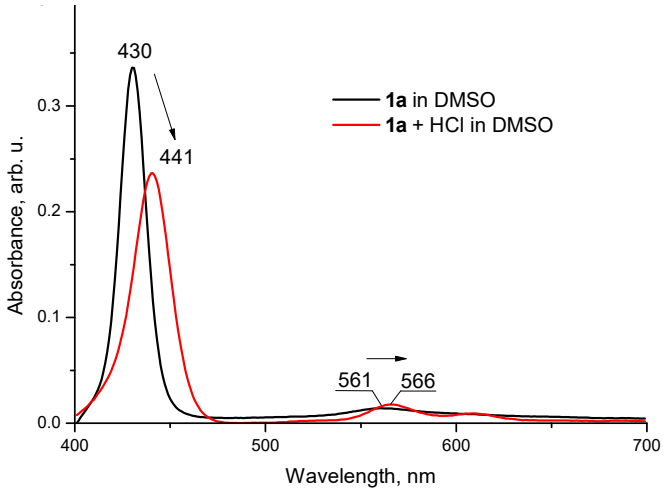

Figure S7. UV-Vis of the initial form **1a** and the protonated form **1a**+**2H**$^+$ in DMSO.

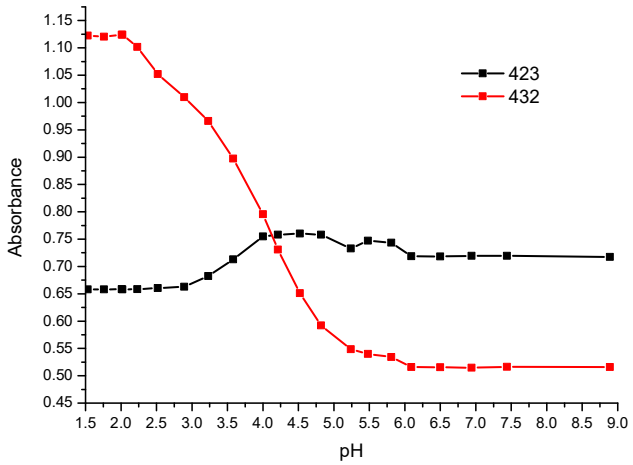

Figure S8. Dependence of optical density at λ = 423 nm (black) and 432 nm (red) on the pH value of the medium (right) during spectrophotometric titration of aqueous solution of **1a** with 0.001M HCl.

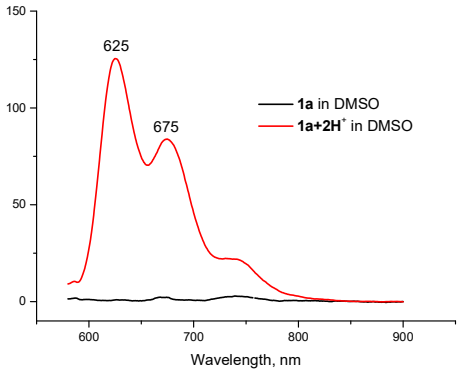

Figure S9. Fluorescence spectra of the initial form **1a** and the protonated form **1a**+**2H**$^+$ in DMSO.

Table S1. Photophysical and photochemical properties of complex **1a** in DMSO.

Complex	λ_{Soret}, λ_Q, nm	λ_F, nm	Φ_F		Φ_Δ
			DMSO	H_2O	
1a	430, 561, 606	-	-	-	0
1a + **2H**$^+$	441, 566, 610	625, 675	0,01	0,05	0.06

Table S2. Selected vertical excitations in the calculated UV-Vis spectra of **1a** and **1a+2H**$^+$ for the r^{2}SCAN-3c geometries calculated by the sTD-DFT method at the CAM-B3LYP/6-31G(d) level of theory in water using solvation model based on density (SMD).

	nm	eV	$F_{osc.}$	Wavefunction
1a				
Q-bands	605.5	2.05	0.03	0.78 H→L; 0.11 H-1→L+1; 0.09 H-3→L+1
	590.5	2.10	0.02	0.79 H→L+1; 0.1 H-1→L; 0.09 H-3→L
	535.0	2.32	0.01	0.62 H-2→L; 0.3 H-3→L+1; 0.06 H-1→L+1
	530.3	2.34	0.01	0.45 H-2→L+1; 0.34 H-3→L; 0.19 H-1→L
Soret band	398.7	3.11	1.51	0.54 H-3→L; 0.27 H-2→L+1; 0.13 H→L+1
	397.1	3.12	1.58	0.57 H-3→L+1; 0.24 H-2→L; 0.13 H→L
1a+2H$^+$				
Q-bands	583.7	2.12	0.05	0.64 H→L; 0.35 H-1→L+1
	576.7	2.15	0.03	0.61 H→L+1; 0.38 H-1→L
Soret band	414.9	2.99	1.21	0.55 H-1→L; 0.35 H→L+1; …
	410.5	3.02	1.36	0.6 H-1→L+1; 0.32 H→L; …