

Features of photoinduced proton transfer in the presence of a polyelectrolyte

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Sodium salt of 2-naphthol-6-sulfonic acid (**1**), disodium salt of 2-naphthol-3,6-disulfonic acid (**2**), disodium salt of 2-naphthol-3,6,8-trisulfonic acid (**3**) (Vekton, Russia) were used in current work. PDDA solutions of the desired concentration were prepared from the 20% stock solution (Sigma-Aldrich, USA) by dilution with deionized water. The experiments were carried out in solutions with pH from 0 to 12.5 at a temperature of 25 ± 2 °C.

The pH value of the solutions was monitored using an Expert-001 pH meter (Econix-Expert, Russia) equipped with an ESK-10601/7 combined pH electrode (Izmeritel'naya Tekhnika, Russia).

The fluorescence spectra of the indicators were recorded on a Cary Eclipse spectrofluorimeter (Agilent Technologies, USA). All measurements were carried out in a quartz cell with an optical path length of 1 cm, the indicator concentration was 4.7×10^{-5} mol·dm⁻³ in all experiments. Registration parameters are given in Table S1.

Table S1 Fluorescence spectra registration parameters.

Sample	$\lambda_{\text{excitation}}$ /nm
1	320
2	324
3	330

Singlet excited state fluorescence decays were measured with Fluotime 300 Time-Correlated Single Photon Counting (TCSPC) UV-IR spectrofluorimeter (Picoquant GmbH, Germany). Emission was detected with a magic angle polarizer to prevent undesired polarization effects. Experimental parameters are shown in Table S2. The obtained fluorescence decay curves were analyzed using FluoFit software (PicoQuant). Model curves of monoexponential decay were fitted on experimental data to obtain τ_0 , τ_0' , which were later used in the calculation of k_1 and k_{-1} .

Table S2 Fluorescence decay registration parameters.

Sample	1		2		3	
	ROH [*]	RO [*]	ROH [*]	RO [*]	ROH [*]	RO [*]
$\lambda_{\text{excitation}}$ /nm	263.7					
Excitation filter bandpass /nm	23.0					
$\lambda_{\text{detection}}$ /nm	364	430	378	464	396	488
Detection filter bandpass /nm	10.8					
Polarisation /°	54.7					
Delay between single measurements /ps	128					
Sync Frequency /Hz	10000340					

Note: ROH^{*} - initial form, RO^{*} - deprotonated form.

If τ_0 and τ_0' are known, then the equation (12) can be used to find the rate constants of the forward and reverse photoprotolytic reactions by measuring the fluorescence spectra at different proton concentrations. An example of the **1** spectra and the straightening plot are shown in Figure 2. Similar dependencies were obtained for **2** and **3** (Figure S1). The trend line equations are shown in Table S3.

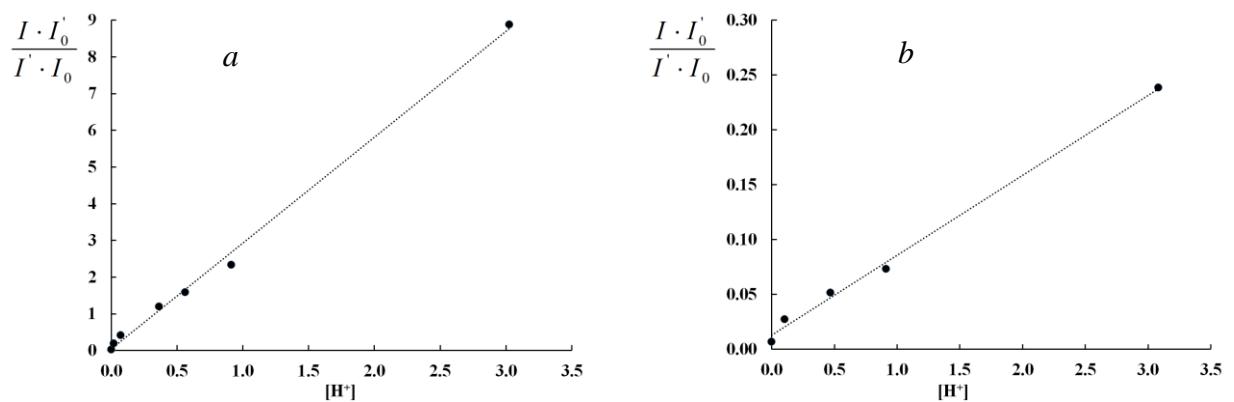


Figure S1 Straightening plot for the dependence of the emission spectrum on pH: (a) – 2, (b) – 3.

Table S3 Trend line parameters for straightening plots.

Sample	Free term	Slope	R^2
1	0.1695	68.48	0.998
2	0.0469	2.919	0.997
3	0.0129	0.0765	0.996