Electronic supplementary materials *Mendeleev Commun.*, 2025, **35**, 179–182

Significant impact of 3-positioned substituent on the fluorescent properties of 5-hydroxyisoquinolones

Alexander Yu. Belyy, Alena D. Sokolova, Rinat F. Salikov, Konstantin P. Trainov, Dmitry N. Platonov and Yury V. Tomilov

Table of Contents

General information

The absorption spectra were recorded on an 'Agilent Cary 60 UV–Vis' spectrophotometer, and the photoluminescence spectra were recorded on a 'Cary Eclipse' spectrofluorometer. All optical studies were performed in low-concentration solutions (1×10^{-4} M for absorption and 5×10^{-6} M for fluorescence) in standard 10×10 mm quartz cells with 90° measurement geometry. All measurements were carried out at room temperature (298 K) in aqueous 0.2 M PBS or in aqueous 0.1 M HCl. DMSO for spectrophotometric titration was dried over calcium hydride and distilled under reduced pressure. The photoluminescence quantum yields were determined by comparing with the known quantum yield of a standard, using the fluorescence measurement method for optically diluted solutions.[S1] A solution of POPOP in ethanol (Φ_F = 0.98)[S2] was used as the standard in all cases.

Mathematical decomposition of fluorescence spectra was performed with a Python script using NumPy and SciPy packages based on four-parametric lognormal functions.[S3]

Quantum chemical calculations were carried out using ORCA 5.0.4 software package.[S4] The difference in total density computed for the ground and excited states *via* PBE0/def2-TZVP/CPCM (water) level of theory. The absorption maxima were obtained *via* PBE0/def2-TZVPP//r^{2}SCAN-3c/CPCM(water) level of theory. The fluorescence maxima were obtained *via* PBE0/def2-TZVPP//PBE0/def2-SVP/CPCM(water) level of theory.

5-Hydroxyisoquinolones **1a–d** were obtained according to the literature procedure.[S5] All other reagents and solvents were commercially available and were used without additional purification.

.

Optical properties of 5-hydroxyisoquinolones

Table S1 Optical properties of 5-hydroxyisoquinolones **1a-d, 2a,b.**

R	R'	λ_{abs} at pH 1, nm (HA)	λ_{abs} at pH 7, nm (A^-)	ε_{max} at pH 1, $M^{-1}\cdot cm^{-1}$	ε_{max} at pH 7, $M^{-1}\cdot cm^{-1}$	λ_{fl} at pH 1, nm	λ_{fl} at pH 7, nm (A^-)	$\Delta\lambda$ at pH1, nm	Stokes shift at pH 1, cm^{-1}	$\Delta\lambda$ at pH 7, nm	Stokes shift at pH 7, cm^{-1}	λ_{fl} decomp., nm (HA)[a]	λ_{0-0}, nm[b] (HA)	λ_{0-0}, nm[c] (A^-),	Φ_F, %[d]	λ_{abs} calc, nm (HA); ΔE_{exp}, eV[e]	λ_{abs} calc., nm (A^-); ΔE_{exp}, eV[e]	λ_{fl} calc., nm (HA); ΔE_{exp}, eV[f]	λ_{fl} calc., nm (A^-); ΔE_{exp}, eV[f]
Me	H	351	392	8 600	11 800	439	462	88	5711	70	3865	417	393	422	11	357; 0.06	376; 0.13	410; 0.05	449; 0.08
Pr^i	H	352	392	9 200	13 000	439	463	87	5630	71	3912	419	395	422	11	358; 0.06	379; 0.11	410; 0.06	447; 0.10
Bn	H	360	391	9100	13 000	436	463	76	4842	72	3977	417	395	423	11	356; 0.04	376; 0.13	411; 0.04	443; 0.12
Ph	H	352	396	8 900	12 600	446	462	94	5988	66	3608	429	398	426	12	361; 0.09	384; 0.10	418; 0.08	435; 0.17
Me	CO_2Me	366[g]	411[g]		15800[h]	430, 524[g]	522[g]	64, 158[g]	4067, 8238[g]	111[g]	5174[g]	430[g]	395[g]	458[g]	41[h]	359; 0.07	403; 0.06	408; 0.16	459; 0.33
Ph	CO_2Me	368[g]	411[g]		18800[h]	442, 525[g]	526[g]	74, 157[g]	4549, 8126[g]	115[g]	5319[g]	442[g]	400[g]	458[g]	45[h]	362; 0.06	409; 0.01	427; 0.10	464; 0.31

[a] obtained from decomposition of fluorescence spectra at pH 1 by four-parameter lognormal function; [b] the intersection points between normalized experimental absorption and decomposed fluorescence bands; [c] the intersection points between normalized experimental absorption and fluorescence bands; [d] determined at pH 7; [e] obtained using PBE0/def2-TZVPP//r^{2}SCAN-3c/CPCM(water); [f] obtained using PBE0/def2-TZVPP//PBE0/def2-SVP/CPCM(water); [g] obtained from ref.[6] [h] obtained from ref.[7]

Fluorescence and absorption spectra of 5-hydroxyisoquinolones

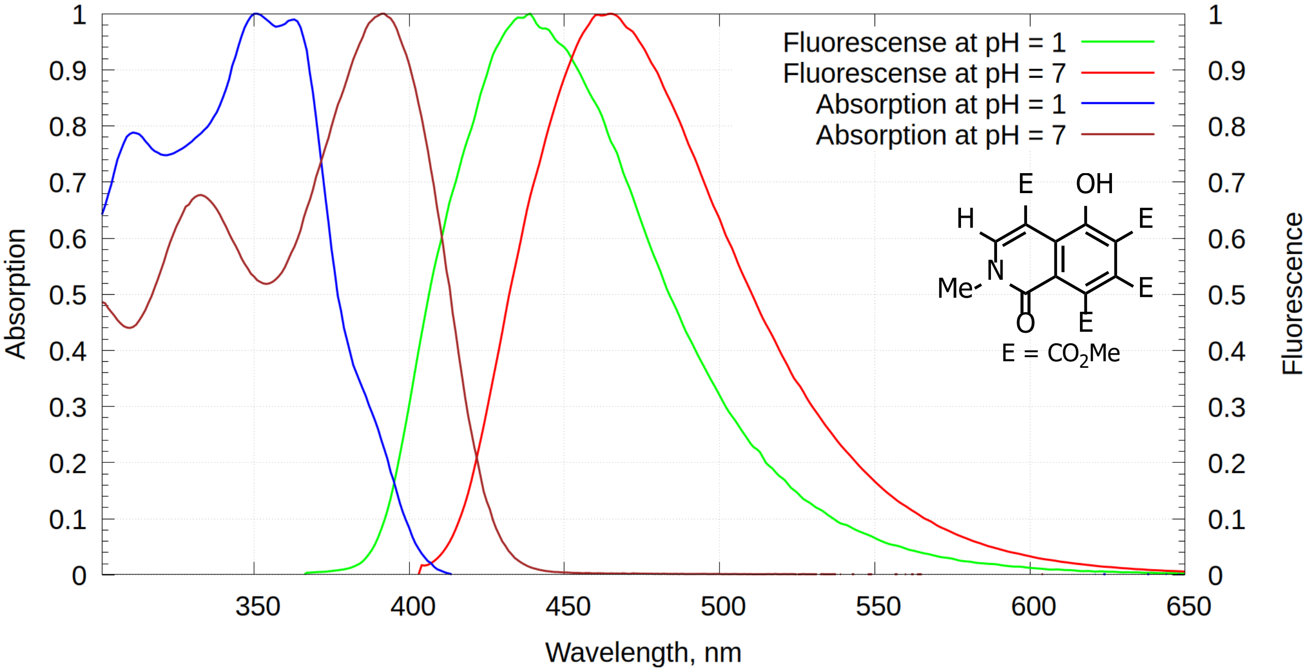

Figure S1 Normalized absorption and fluorescence spectra for **1a**.

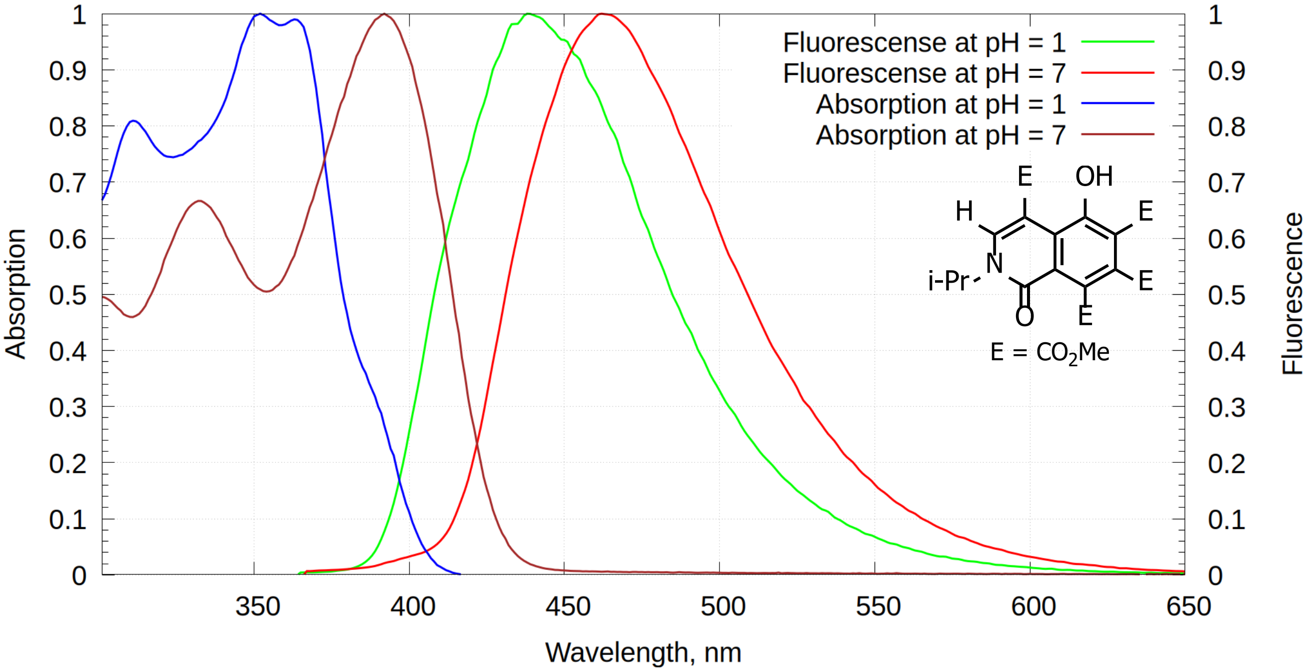

Figure S3 Normalized absorption and fluorescence spectra for **1c**.

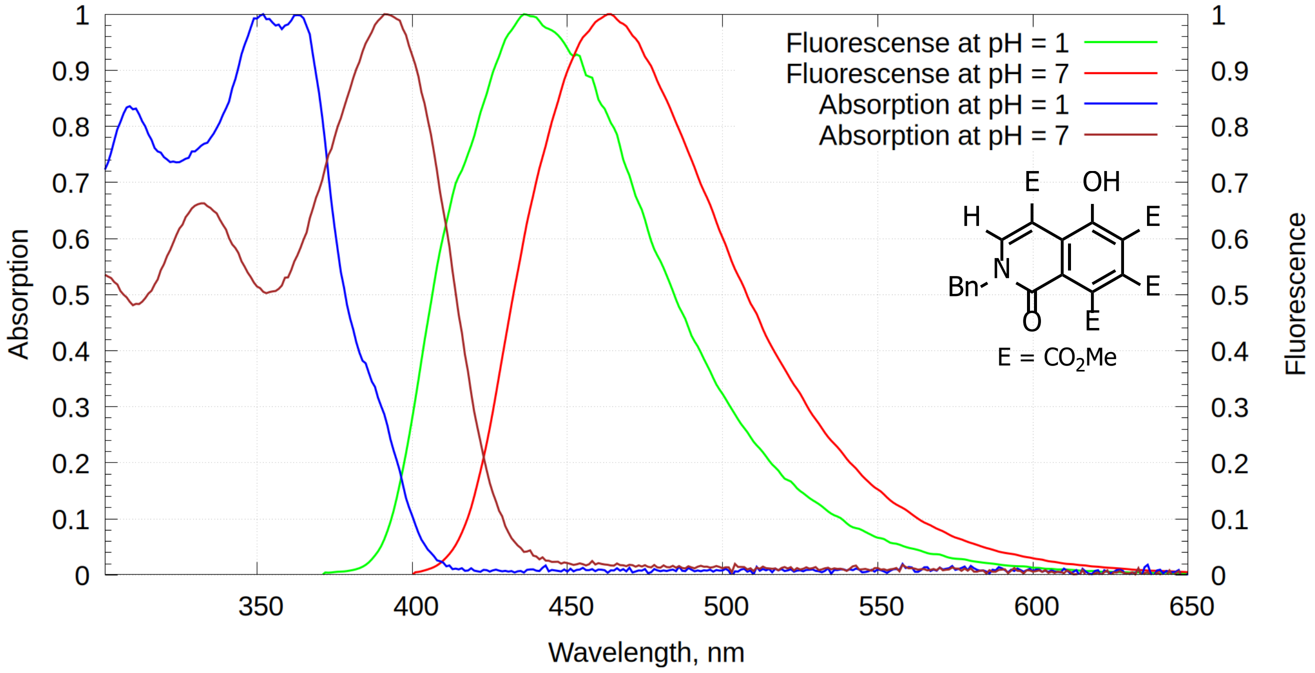

Figure S4 Normalized absorption and fluorescence spectra for **1d**.

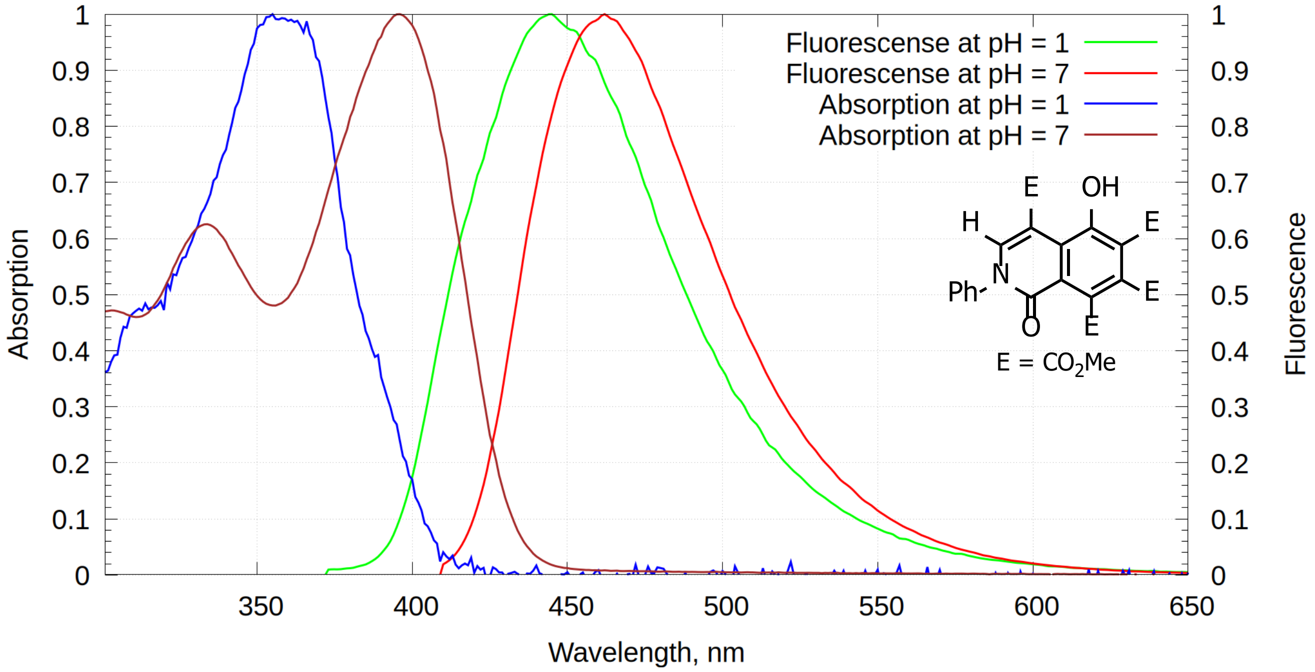

Figure S5 Normalized absorption and fluorescence spectra for **1b**.

Evaluation of 0–0 transition wavelengths

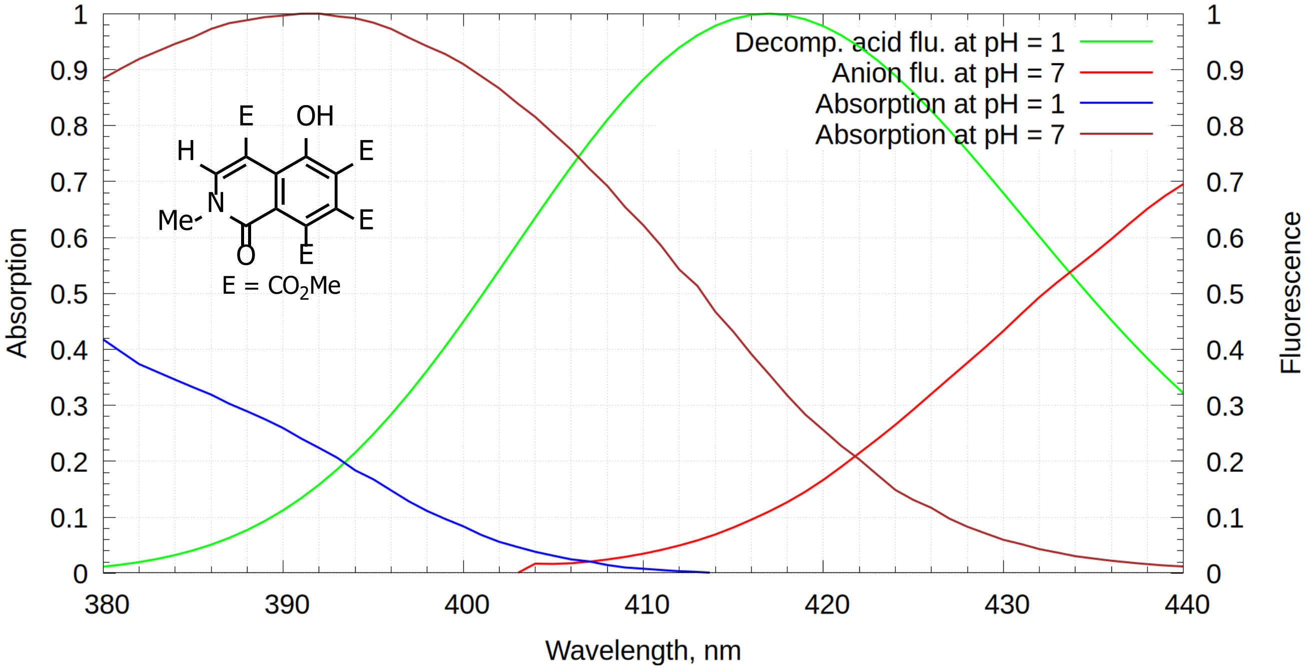

Figure S6 Intersections between normalized absorption and fluorescence spectra of neutral and anionic forms of **1a**.

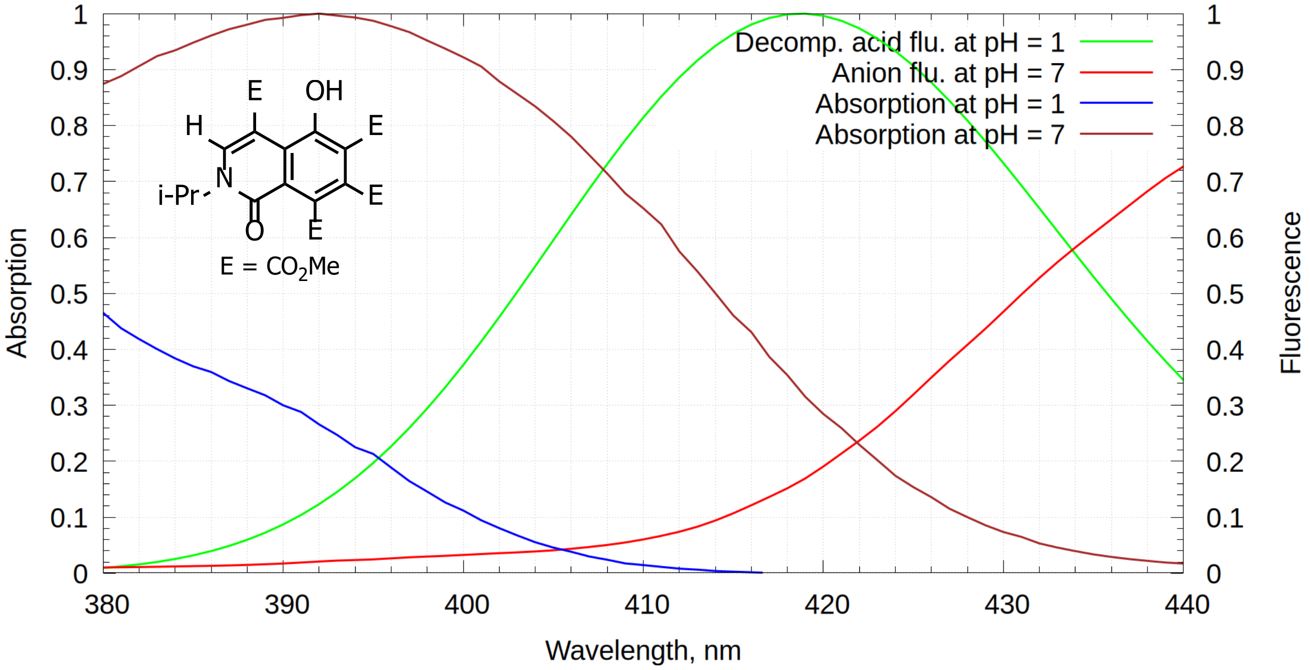

Figure S7 Intersections between normalized absorption and fluorescence spectra of neutral and anionic forms of **1c**.

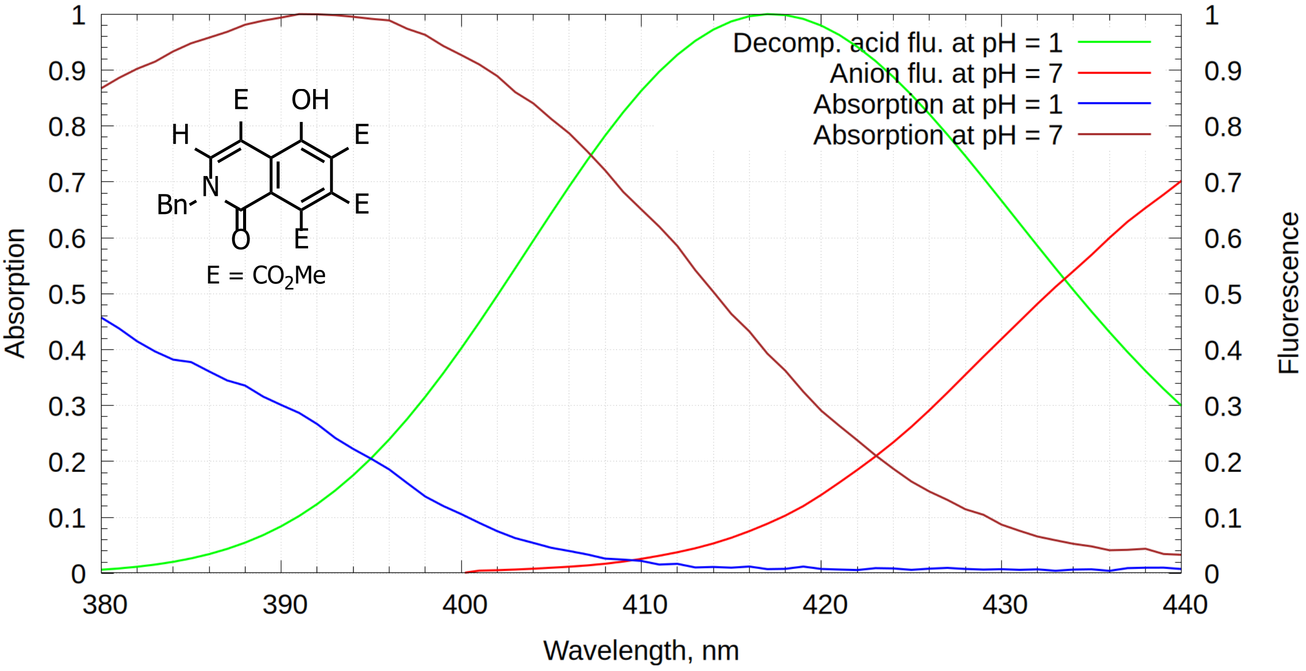

Figure S8 Intersections between normalized absorption and fluorescence spectra of neutral and anionic forms of **1d**.

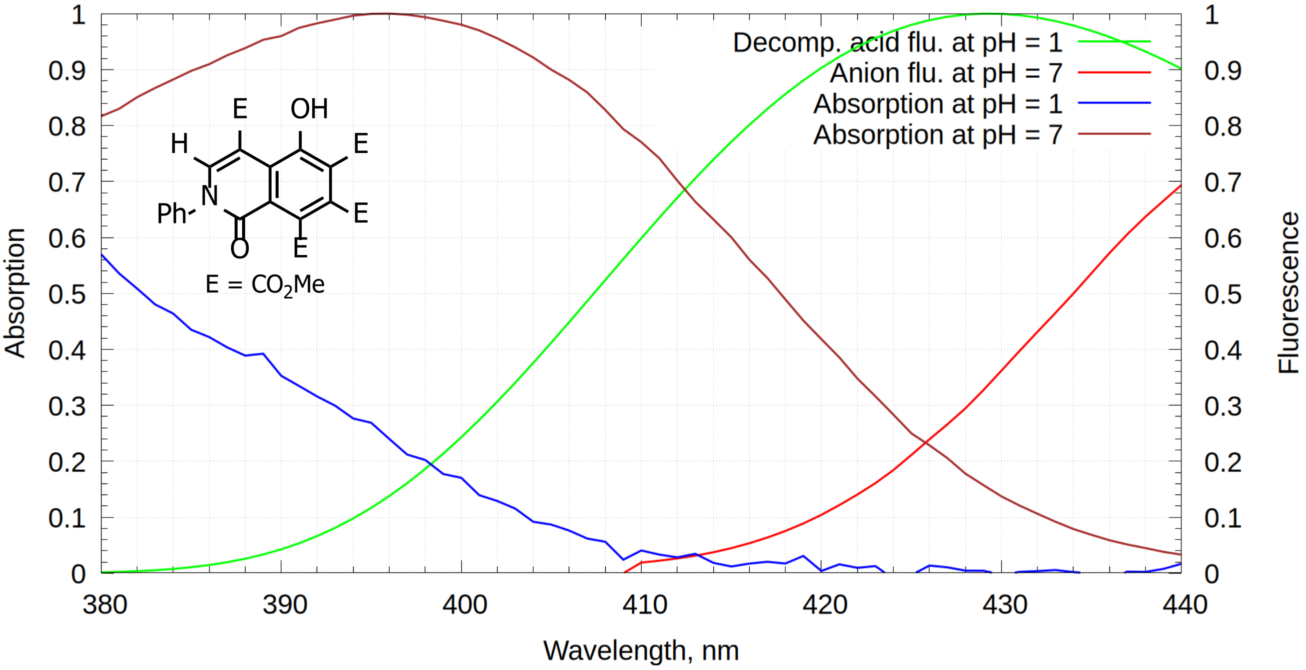

Figure S9 Intersections between normalized absorption and fluorescence spectra of neutral and anionic forms of **1b**.

Spectrophotometric titration of 5-hydroxyisoquinolone 1a

To determine the acidity of isoquinolones in their ground state, we utilized spectrophotometric titration as a straightforward method. Specifically, we measured the correlation between the optical density at the absorption maximum and the pH of the medium for isoquinolone **1a**. We selected the basic maximum (392 nm) as it more accurately reflects the concentration of the anion, whereas the acidic maximum overlaps with the absorption band of the anion and therefore does not provide an accurate concentration of the acidic form.

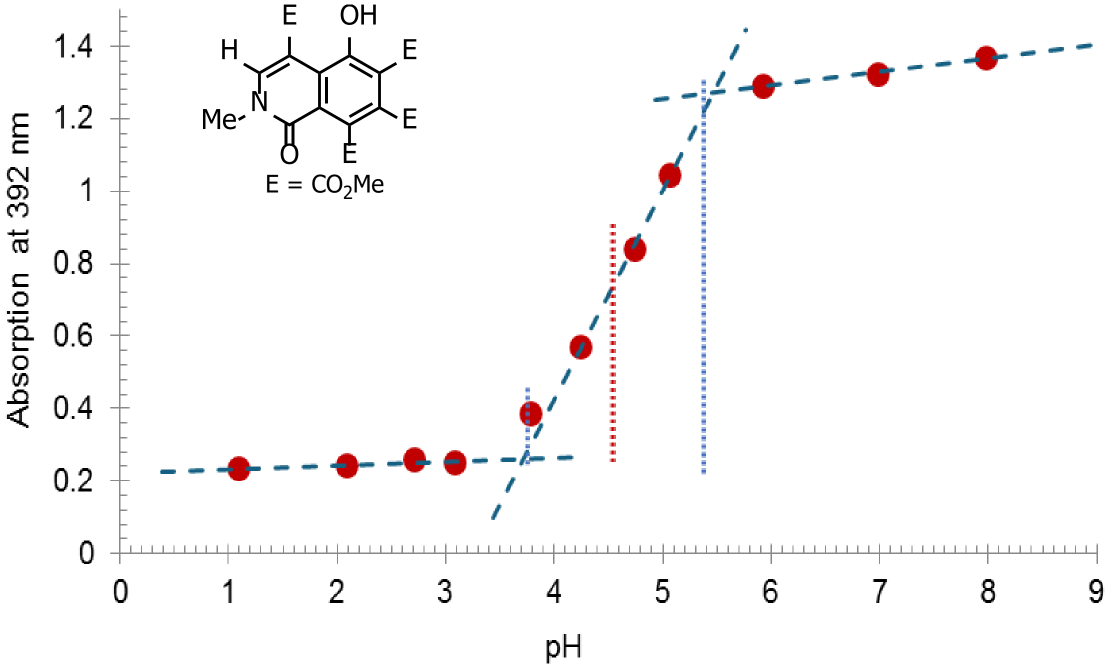

Figure S10 Spectrophotometric titration curve for **1a**.

Evaluation of levels of theory accuracy

The presence of ESCT often reduces the accuracy of TDDFT calculations. Thus, for the estimation of the fluorescence maximum of **2a** anion various TDDFT functionals and the post-HF method STEOM-DLPNO-CCSD were tested. In all cases the geometry was obtained using S1 PBE0/def2-svp. The results are presented in Table S2.

Table S2 The evaluation of levels of theory accuracy for the estimation of fluorescence maximum of compound **2a** in the anionic form in water.

Functional	**λ_{flu}, nm**	**Error, eV**
ωB97X/def2-tzvpp	414	0.62
M062X/def2-tzvpp	424	0.55
cam-B3LYP/def2-tzvpp	431	0.50
PBE0/def2-tzvpp	459	0.33
B3LYP/def2-tzvpp	471	0.26
STEOM-DLPNO-CCSD/def2-tzvp	501	0.10

The color indicates the deviation from the experiment: <0.1eV, <0.3eV, >0.3eV.

The results depicted in the Table S2 reveal that, within the realm of TDDFT functionals, only B3LYP demonstrates satisfactory performance, while other functionals yield subpar outcomes. Surprisingly, even the CAM-B3LYP functional, tailored to account for charge transfer effects, fails to deliver promising results. Additionally, a consistent blue shift is evident across all instances. Although the high-level post-Hartree–Fock method performs commendably, it is important to note that its computational cost is nearly two orders of magnitude higher in terms of processing time.

References

S1 G. A. Crosby and J. N. Demas, *J. Phys. Chem.*, 1971, **75**, 991; https://doi.org/10.1021/j100678a001.

S2 I. Berlman, *Handbook of Florescence Spectra of Aromatic Molecules*, 2nd ed., Elsevier, 1971; https://doi.org/10.1016/B978-0-12-092656-5.X5001-1.

S3 D. B. Siano and D. E. Metzler, *J. Chem. Phys.*, 1969, **51**, 1856; https://doi.org/10.1063/1.1672270.

S4 F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2022, **12**, e1606; https://doi.org/10.1002/wcms.1606.

S5 A. Yu. Belyy, A. D. Sokolova, R. F. Salikov, V. V. Litvinenko, D. N. Platonov and Yu. V. Tomilov, *Mendeleev Commun.*, 2025, In Press.

S6 R. F. Salikov, A. Y. Belyy, K. P. Trainov, J. A. Velmiskina, M. G. Medvedev, V. M. Korshunov, I. V. Taydakov, D. N. Platonov and Y. V. Tomilov, *J. Photochem. Photobiol. A*, 2022, **427**, 113808; https://doi.org/10.1016/j.jphotochem.2022.113808.

S7 A. Y. Belyy, D. N. Platonov, R. F. Salikov, K. P. Trainov, M. G. Medvedev, Y. N. Luponosov, E. A. Svidchenko and Y. V. Tomilov, *Dyes Pigm.*, 2021, **187**, 109107; https://doi.org/10.1016/j.dyepig.2020.109107.