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Supplementary information

Dynamics of Excited State Proton Transfer in Nitro Substituted 10-Hydroxybenzo[h]quinolines

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Analysis of Stationary Spectra:

The procedure developed by Barone at al. [1] allows to calculate molecular absorption and fluorescence spectra and their vibrational progressions using Franck−Condon factors and the Duchinsky matrix for mixing of the normal modes . Unfortunately this approach cannot predict the spectra of the enol tautomers of **2** and **3**, due to the non-planarity of **E***.[2] The spectra of the keto tautomers, however, were simulated by the method and those of **2** are shown in Figure S1. According to the band decomposition procedure for analyzing tautomeric mixtures[3] the long-wavelength band of the keto form consists of two sub-bands (Figure S1a). They are not evident when the spectra of the tautomeric mixture are visually inspected (for instance Figure 1a), but can be seen by fourth derivative spectra. Comparing the shape of the pure **2K** absorption spectrum obtained in this way (Figure S1a) with the theoretical calculations (Figure S1b), a strong similarity can be seen. The experimental (Figure 1b) and the simulated (Figure S1b) emission spectrum agree also well with each other.

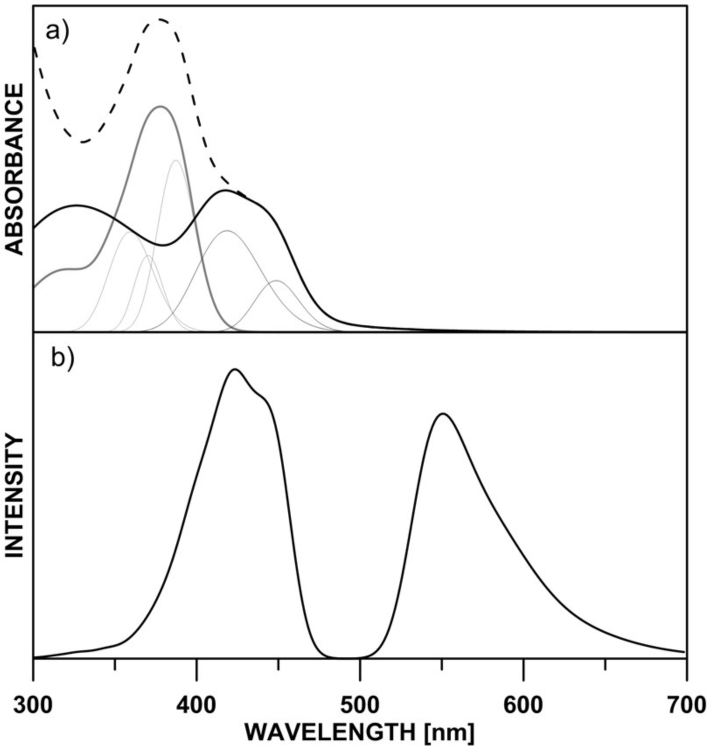

Figure S1. a) Absorption spectrum of **2** in acetonitrile (dashes) and the spectra of the enol (grey solid line) and keto (black solid line) form obtained by band decomposition[3,4]. b) Calculated absorption (left) and emission (right) spectrum of **2K** in acetonitrile.

Theoretical calculations:

The available experimental information about the molar fractions of the tautomers in the ground state (ΔG values) and the information about the mechanism of the ESIPT allow to explain the observed variation in the spectroscopy of the compounds and to verify the theoretical calculations. The relative stability of the tautomers is summarized in Table S1 as predicted by the calculations in the ground state and in some cases also in the excited state. Although not shown in the table all used DFT functionals predict that in acetonitrile HBQ exists in the ground state only as enol tautomer and in the excited state as keto form. This is in line with the calculations by B3LYP/6-311þþG(d,p)[5] and recently used DFT corrected complete active space configuration interaction methods[6]. However, depending on the method and solvation model an ESIPT barrier in the S_0 and S_1 state is predicted in the literature using B3LYP/TZVP in gas phase[7] and in methylcyclohexane[8]. The situation for **2** and **3** seems to be even more complicated analyzing the results from Table S1. The use of B3LYP predicts reasonably well the situation for **2** in the ground state (comparing to the experiment), while it strongly overestimates the stability of **3K**. In the excited state a barrierless PT is predicted for **3** if B3LYP/TZVP is applied, while the electronically excited enol form of **2** (**2E***) is found to be substantially lower in energy than the electronically excited proton transfer form (**2K***) and ESIPT in **2** is predicted to be absent. If NM12SX and BHandH are used, the energies of **2E** and **3K** are overestimated. In the case of M06-2X, independent on the basis set, only the enol form exists in ground state for **2** (contrary to the experiment), while the tautomeric mixture of **3** is perfectly reproduced. Møller-Plesset perturbation and coupled-cluster theories practically exclude the existence of a keto tautomer in both compounds. An additional difficulty arises from the inability of the methods listed in Table S1 to describe the experimental situation in **2,** neither in S_0 nor in S_1. According to the M06-2X functional the enol form is more stable in both the ground and the excited state. The relative stability of **2E*** versus **2K*** is reduced going from the TZVP to the def2TZVP basis set, but at the same time the presence of nitro group(s) does not allow to perform optimizations of the transition states with the latter. Obviously the ground and excited state PT in **2** cannot be correctly described by the used levels of theory. In the manuscript compound **3** will be considered as representative example for the nitro substitution based on the similarity in the spectral behavior of **2** and **3**. Under this assumption the use of M06-2X/TZVP is a computationally affordable method for a theoretical description of the processes. The details are presented in Table S1.

Table S1. Relative energies (in kcal/mol) of the tautomers of **2** and **3** in the ground state in acetonitrile as obtained at various levels of theory.

Compound	Theory	ΔE	
		E	**K**
2	experiment (ΔG value)[2]	0.0	1.03
	M06-2X/TZVP	0.0 (0.0)*	4.86 (3.03)*
	M06-2X/def2TZVP	0.0 (0.0)*	4.70 (1.09)*
	M06-2X/def2QZVP	0.0	4.72
	M06-2X/6-311++G**	0.0	5.09
	M06-2X/cc-pVTZ	0.0	5.13
	B3LYP/TZVP	0.0 (0.0)*	1.78 (8.46)*
	B3LYP/6-311++G**	0.0	1.63
	MN12SX/TZVP	0.0	3.84
	BHandH/TZVP	0.0	3.34

	MP2/TZVP	0.0	-**
	MP2/TZVP//M06-2X/TZVP	0.0	7.48
	MP4/TZVP//M06-2X/TZVP	0.0	6.22
	CCSD(T)/TZVP//M06-2X/TZVP	0.0	6.81
3	experiment (∆G value)[2]	0.0	0.62
	M06-2X/TZVP	0.0 (1.36)*	0.58 (0.0)*
	M06-2X/def2TZVP	0.0 (2.76)*	0.74 (0.0)*
	M06-2X/def2QZVP	0.0	0.67
	M06-2X/6-311++G**	0.0	0.75
	M06-2X/cc-pVTZ	0.0	1.12
	B3LYP/TZVP	1.97 (-**)*	0.0 (0.0)*
	B3LYP/6-311++G**	2.14	0.0
	MN12SX/TZVP	0.43	0.0
	BHandH/TZVP	0.34	0.0
	MP2/TZVP	0.0	3.82
	MP2/TZVP//M06-2X/TZVP	0.0	3.65
	MP4/TZVP//M06-2X/TZVP	0.0	2.35
	CCSD(T)/TZVP//M06-2X/TZVP	0.0	2.72

* in excited state; ** no stable form found.

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