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Fluorescent benzimidazo[1,2-a]quinolines: Synthesis, spectroscopic and computational studies of protonation equilibria and metal ion sensitivity

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Supplementary Information

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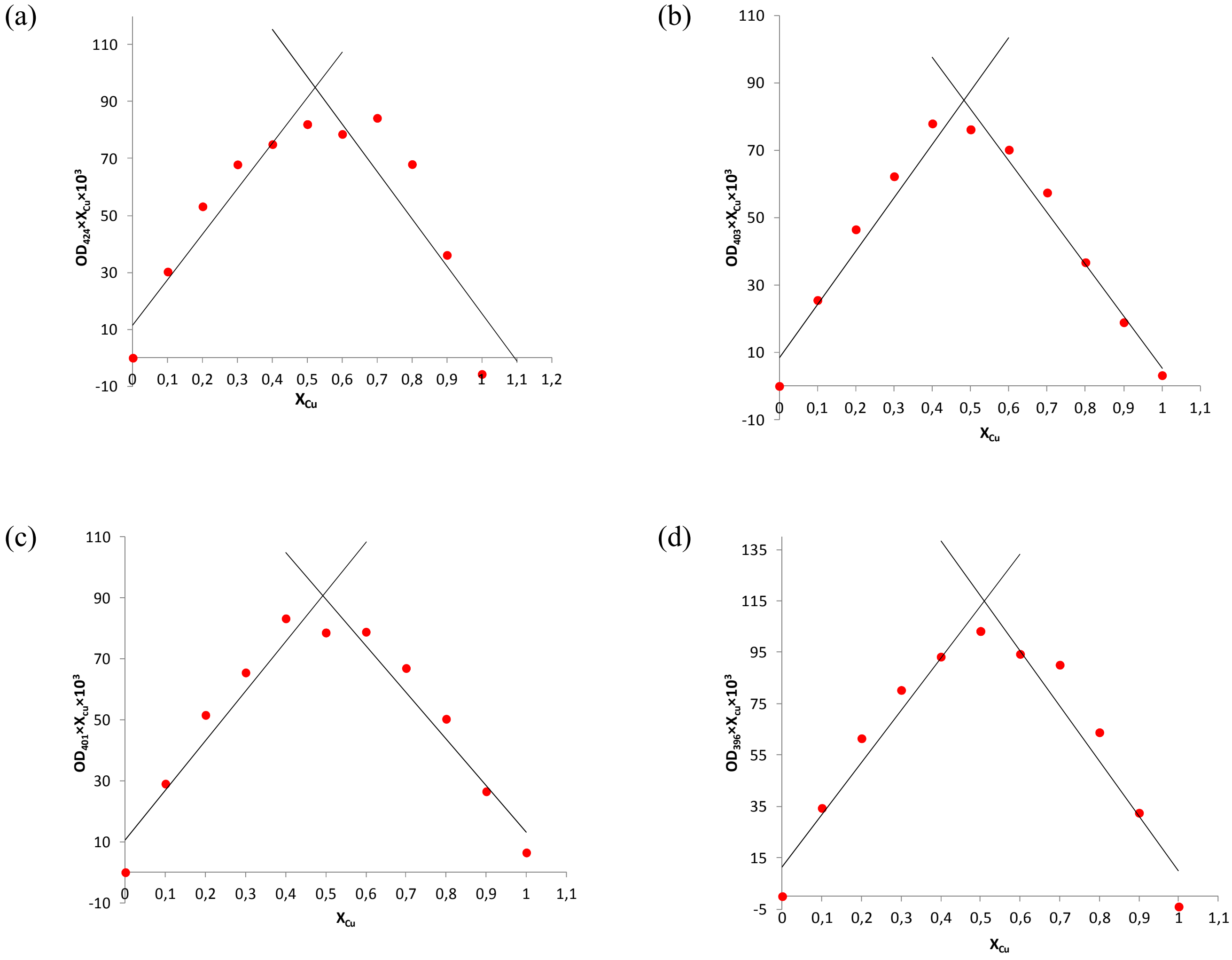


Figure S1. Job's plot for the determination of the stoichiometry of **3** (a), **4** (b), **5** (c) and **6** (d) with the Cu^{2+} ions in the complex. The total concentration of compounds **3**–**6** and Cu^{2+} is 2×10^{-5} mol dm^{-3}.

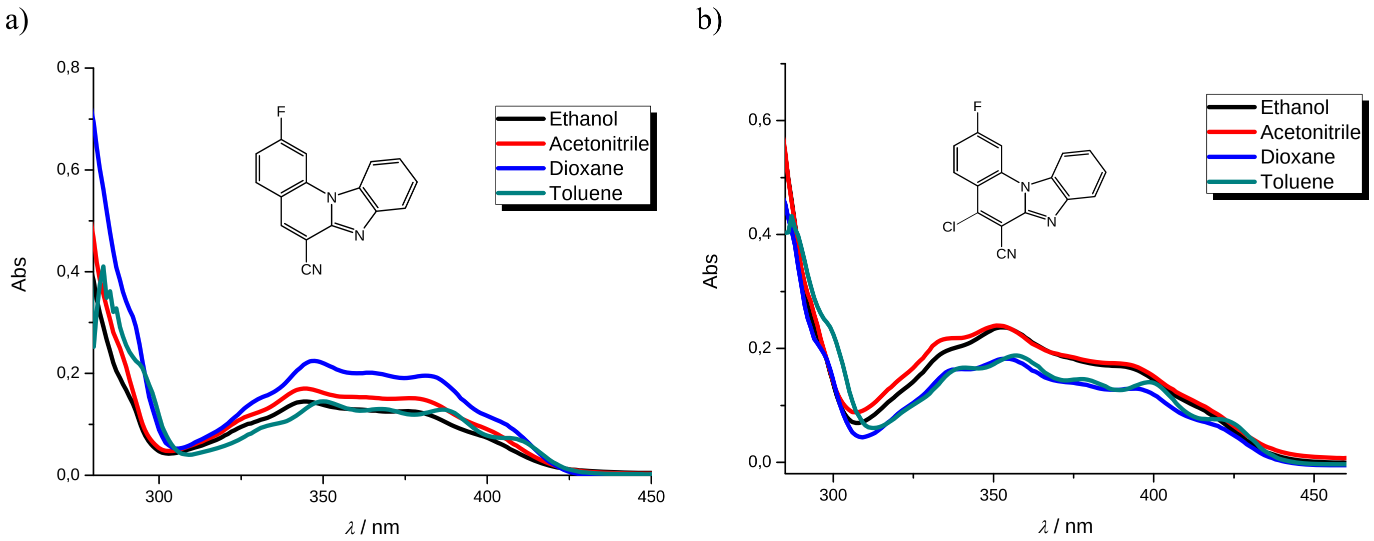


Figure S2. UV-Vis spectra recorded in ethanol, acetonitrile, dioxane and toluene at concentration of 2×10^{-5} mol dm^{-3} of **1** (a) and **2** (b).

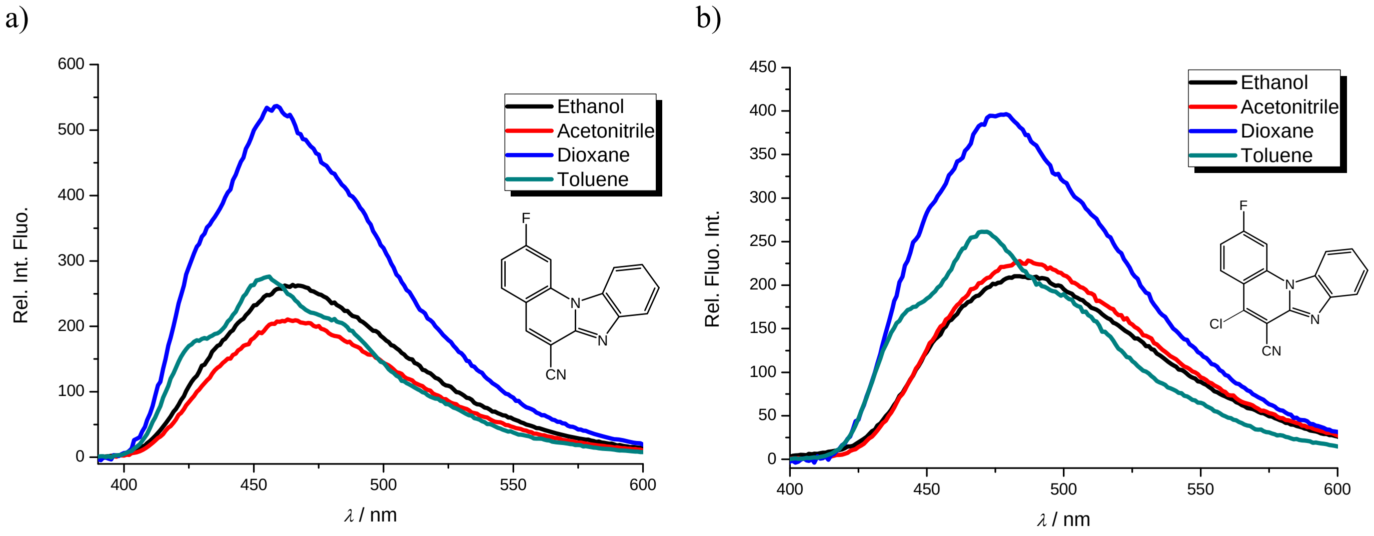


Figure S3. Fluorescence emission spectra in ethanol, acetonitrile, dioxane and toluene at concentration of 1×10^{-7} mol dm^{-3} of **1** (a) and **2** (b).

Table S1. Electronic absorption and fluorescence emission data of parent compounds **1** and **2** recorded at the same concentration in four organic solvents.

compound	**1**				**2**			
solvent[a]	Eth	Acn	Dxn	Tol	Eth	Acn	Dxn	Tol
λ_{max} (nm)	378	379	383	408	390	390	396	423
	343	344	346	387	352	352	353	399
	271	267	270	349	334	334	335	378
	260	259	261		269	272	273	357
	246	244	251		262	263	263	335
					248	248	252	
ε x 10^3 (dm^3 mol^{-1} cm^{-1})	6.2	7.5	9.7	3.5	8.6	8.6	6.3	3.6
	7.2	8.4	11.1	6.4	11.9	11.9	8.9	7.3
	26.3	33.3	44.2	7.3	9.7	10.9	8.2	7.4
	25.3	31.8	43.2		36.2	36.5	27.5	9.2
	24.4	31.1	43.3		36.8	35.7	27.2	8.2
					39.6	39.6	32.6	
λ_{emiss} (nm)[b]	465	464	458	429	486	486	476	443
				454				470
				483				501
relative fluorescence intensity	265	208	538	179	210	225	397	173
				275				262
				206				186
Φ	0.3361	-	-	-	0.2250	-	-	-

[a] Abbreviations Eth, Acn, Dxn and Tol correspond to ethanol, acetonitrile, dioxane and toluene, respectively.

[b] The underlined wavelength values correspond to the most pronounced maximum in the visible region.

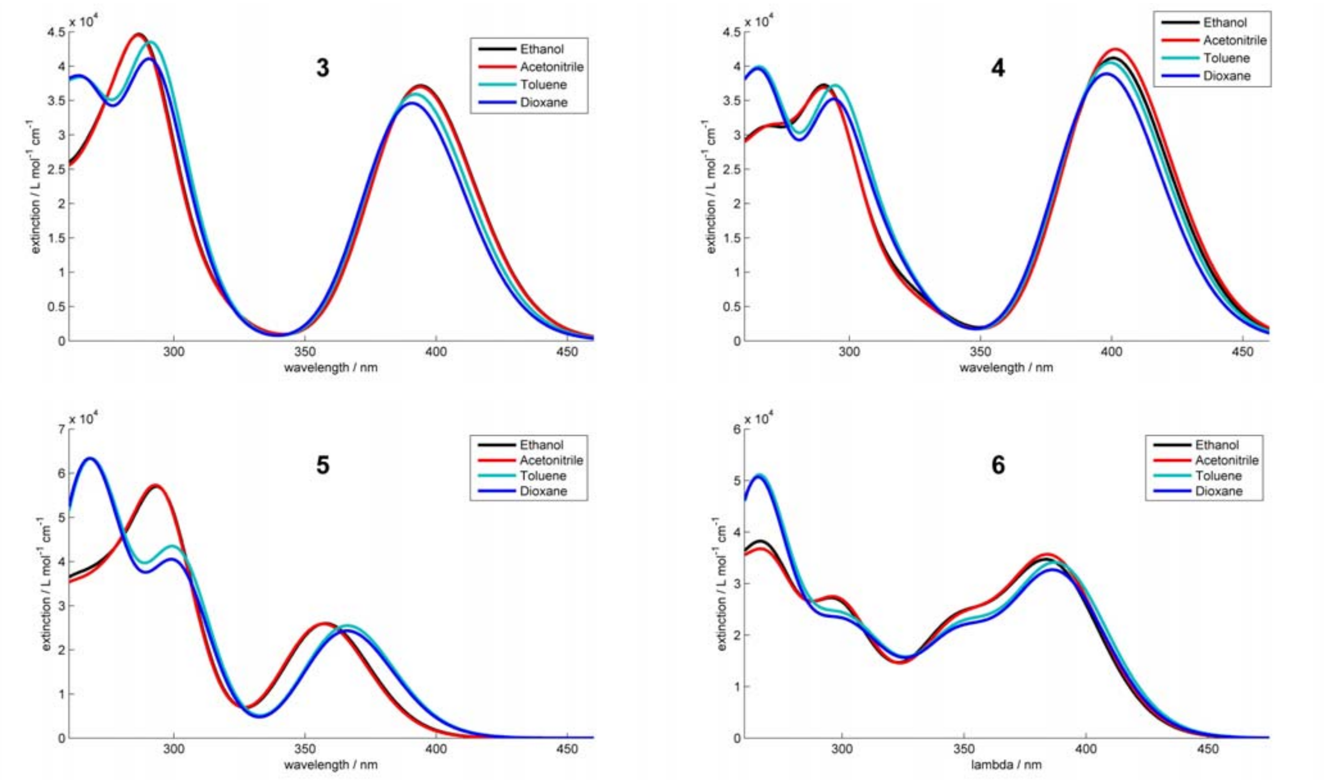
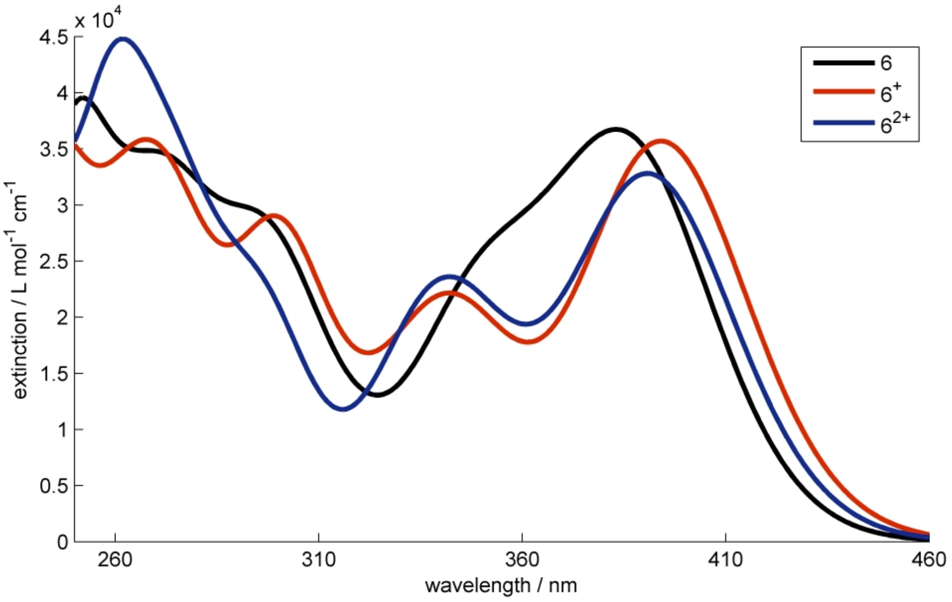


Figure S4. TD-DFT calculated UV/Vis spectra of molecules **3–6** in various solvents obtained at the (IEF–PCM)/M06/6–31+G(d) level of theory. The spectra are simulated by convolution of the pure vertical transitions with the Gaussian distribution function and a plausible standard deviation at 1.8×10^{-4} nm^{-1} (0.223 eV).



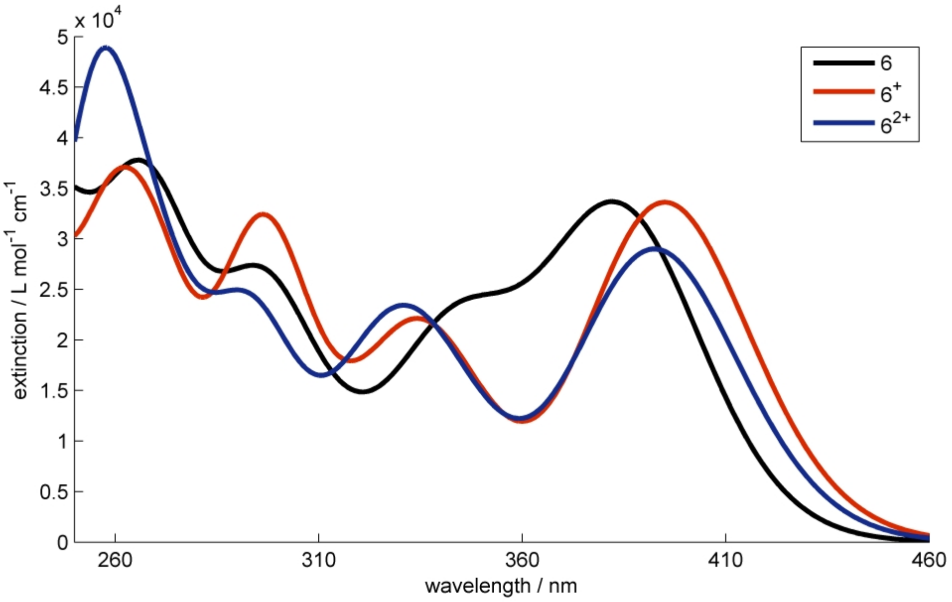
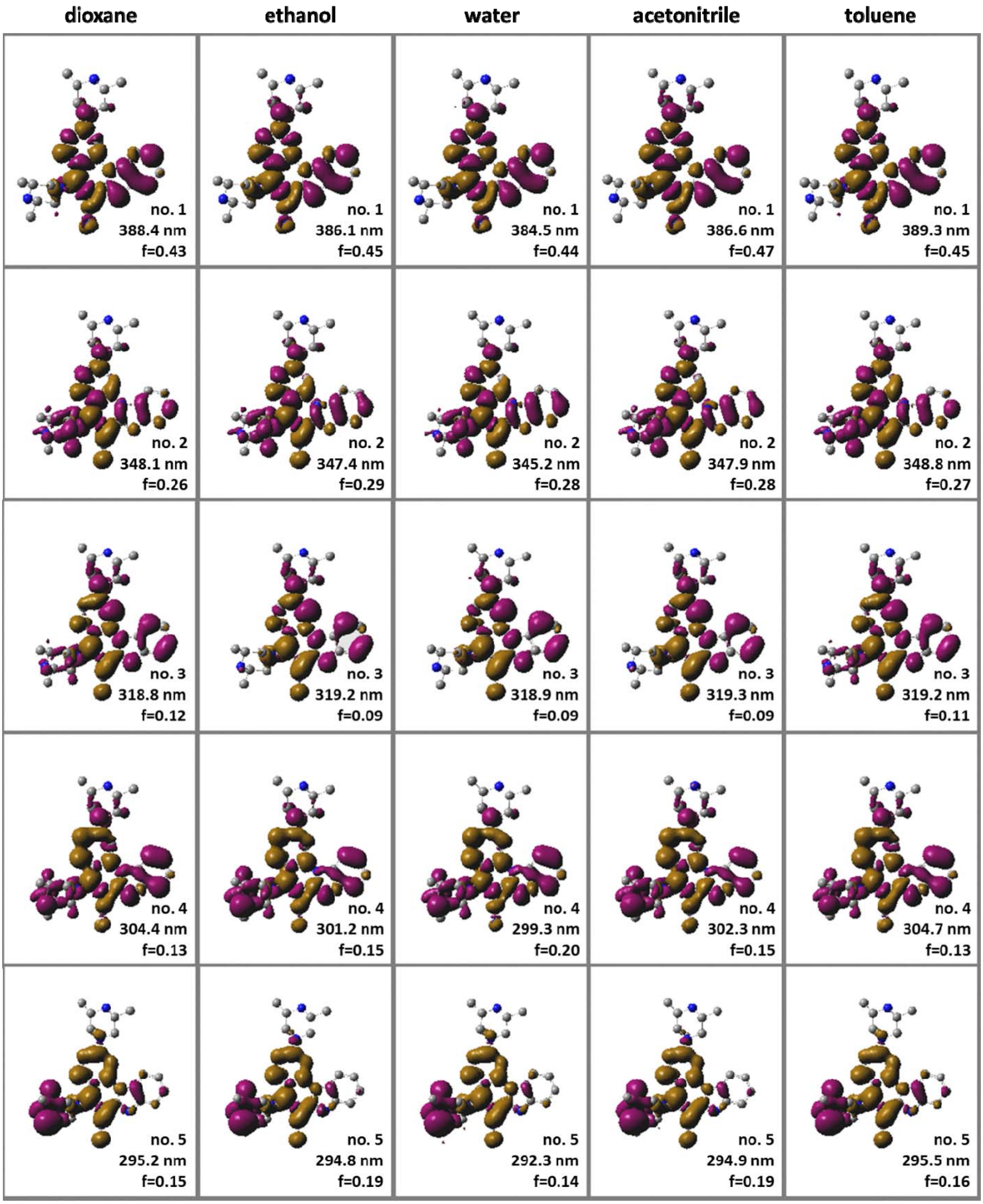


Figure S5. TD-DFT calculated UV/Vis spectra of **6** and its monoprotonated (**6**$^+$) and diprotonated (**6**$^{2+}$) derivatives in water obtained at the (IEF–PCM)/M06/6–311++G(2d,2p) (top) and (IEF–PCM)/M06/6–31+G(d) (bottom) levels of theory. Note that the augmentation of the basis set does not bring qualitative differences in the results. The spectra are simulated by convolution of the pure vertical transitions with the Gaussian distribution function and a plausible standard deviation at 1.8×10^{-4} nm^{-1} (0.223 eV).



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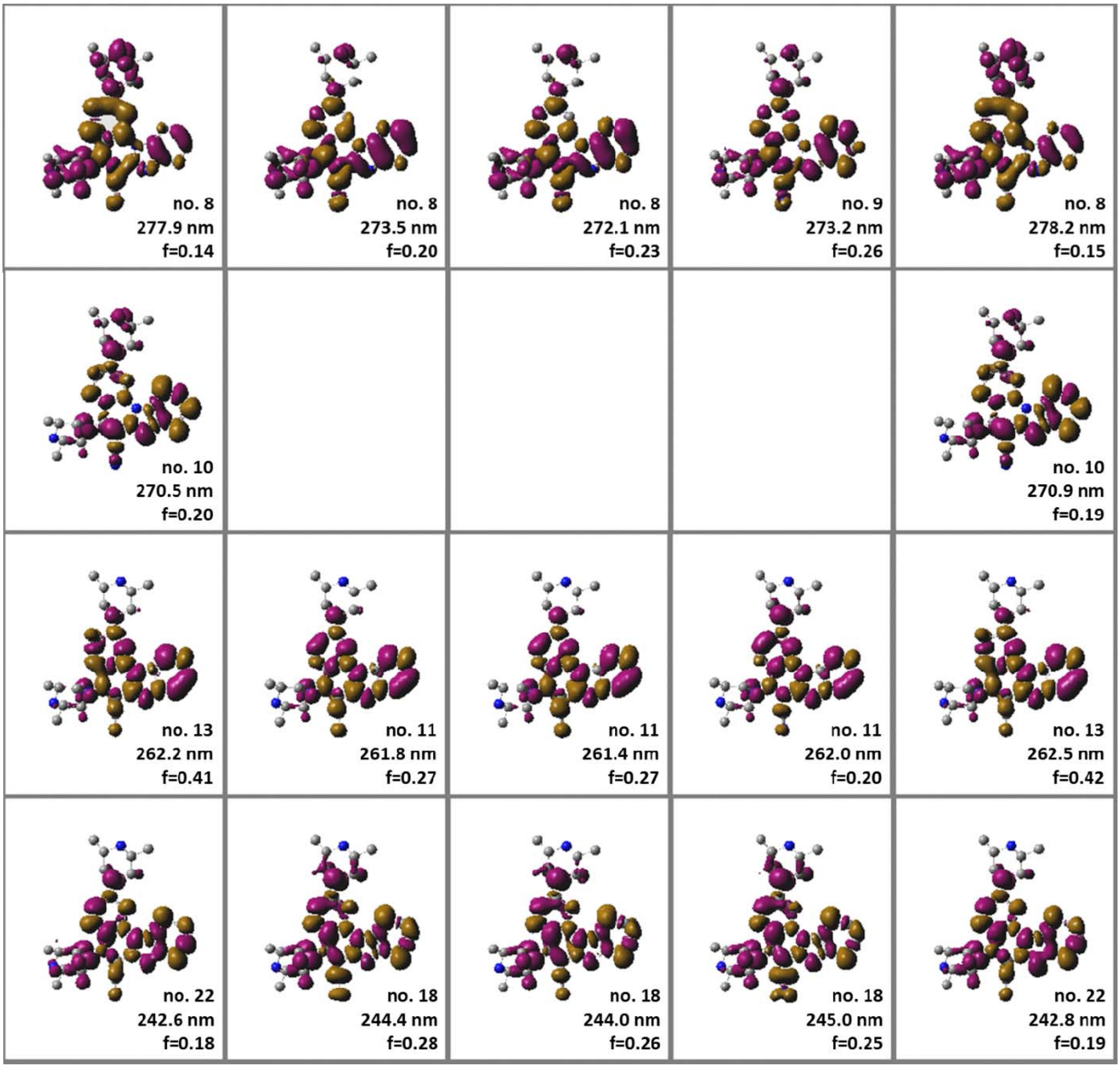

Figure S6. Difference densities of the lowest active excited states of **6**, calculated for various solvents. Electron enriched regions are coloured in purple, and those depleted in charge in drab. Excitation wavelength (in nm) is written below the ordinal number of the excited state, while *f* denotes the oscillator strength. The excited states are calculated by the TD-DFT method at the (IEF–PCM)/M06/6–31+G(d) level of theory. The molecular skeleton is oriented in the same way throughout the text (with the nitrile group pointing downwards).

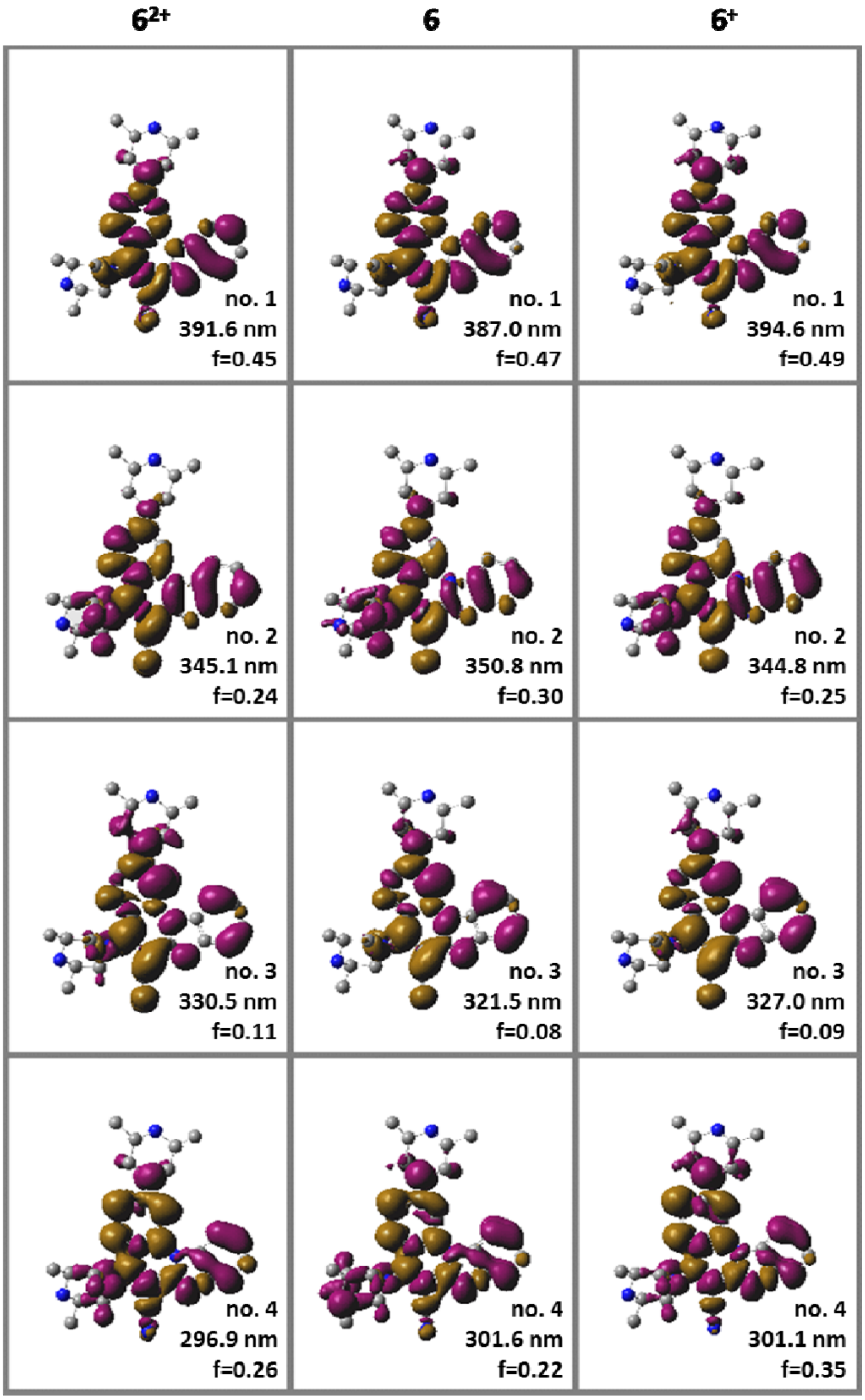

Figure S7. Difference densities of the lowest active excited states of **6** and its monoprotonated (**6**$^+$) and diprotonated (**6**$^{2+}$) derivatives in water. Electron enriched regions are coloured in purple, and those depleted in charge in drab. Excitation wavelength (in nm) is written below the ordinal number of the excited state, while *f* denotes the oscillator strength. The excited states are calculated by the TD-DFT method at the (IEF–PCM)/M06/6–31+G(d) level of theory. The molecular skeleton is oriented in the same way throughout the text (with the nitrile group pointing downwards).

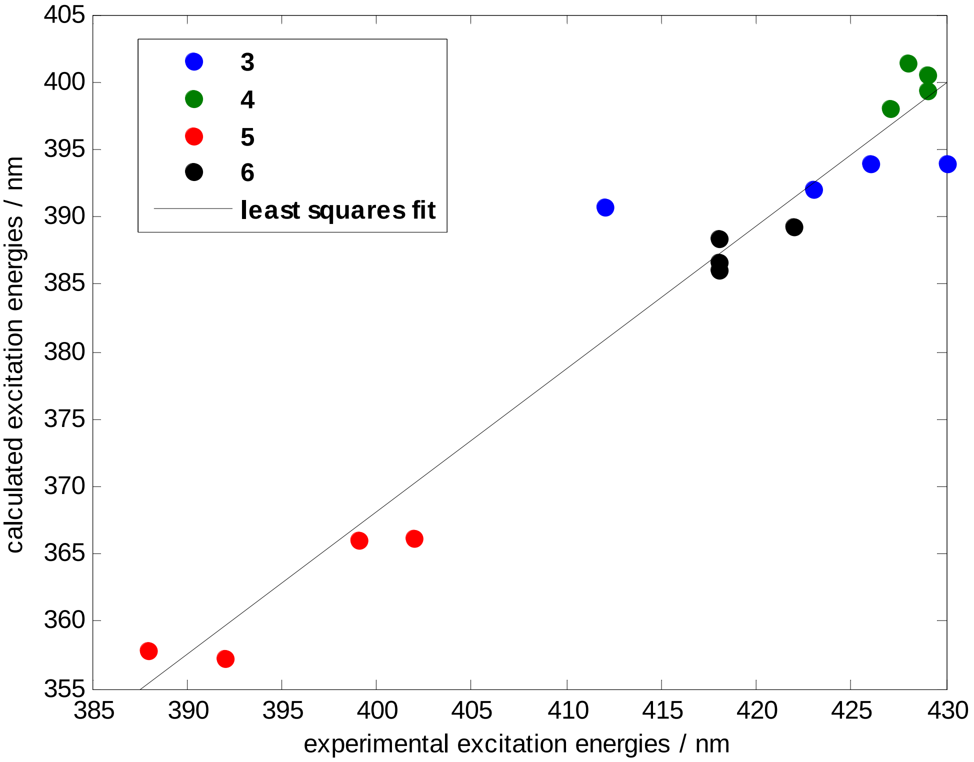

Figure S8. Correlation between the calculated and experimental lowest excitations for systems **3–6** in different solvents. Only the first excitation energies are shown (the solvents are not labeled). Linear regression reveals a reasonable correlation ($\lambda_{\mathrm{CALC}} = 1.058\cdot\lambda_{\mathrm{EXP}} - 55.07$) with the regression coefficient of $R^2 = 0.94$.