SI0 UV-vis absorption spectra and emission response of 6MQz and 6MQc

The absorption and emission spectra of the zwitterion 6MQz and its protonated analogue 6MQc are shown in Fig. SI0. The data are collected in acetonitrile.

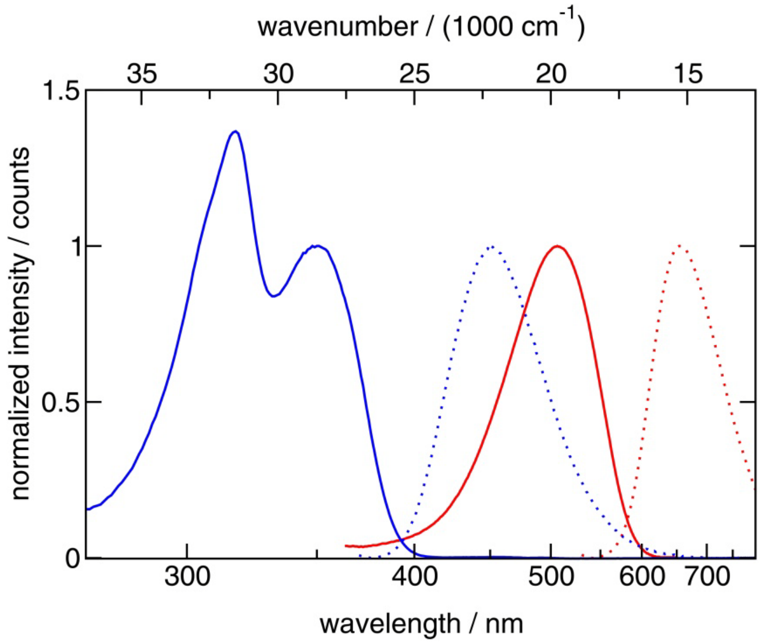

Fig. SI0: Normalized absorption (solid) and emission spectra (dashed) of the zwitterionic 6MQz (red, λex = 510 nm) and the protonated 6MQc (blue, λex = 360 nm) in acetonitrile.

There is no significant overlap between the two species. Therefore, the signals can be plotted and addressed separately what enables distinct quantitative analysis. The Stokes shift in acetonitrile is about 145 nm for 6MQz and 95 nm for 6MQc.

SI1 Vibrational modes and chemical structure of 6MQz, intermediate and 6MQc in acetonitrile

As an assumption acetonitrile is the only known solvent which facilitates the formation of an intermediate during protonation. MIR spectra of 6MQz with different degree of protonation are measured to figure out characteristic vibration modes of the intermediate. Measured vibrations are compared to calculated frequencies to clarify the chemical structures.

Experimental details

Chemicals
A stock solution 6MQz in dry acetonitrile was prepared under argon atmosphere. Therefore 30 mg 6MQz were dissolved in 7.264 g acetonitrile to give a solution of 20.24 mmol^{-1}. We chose such unusual small concentration to ensure the comparability to the UV-vis samples. A stock solution of trifluoromethane sulfonic acid (TFMSA) was prepared as well (5.779 g acetonitrile/30 mg TFMSA). The exact concentration of the acid was measured by acid base titration with NaOH to be 27 mmol l^{-1}. The stock solutions were mixed to give samples of 1.2, 1, 0.8, 0.6, 0.5, 0.4, 0.2, 0.1 and 0 mole fractions TFMSA.

MIR
Instrument: Vertex 80, MCT detector, transmission mode, 50 µm path length

Figures

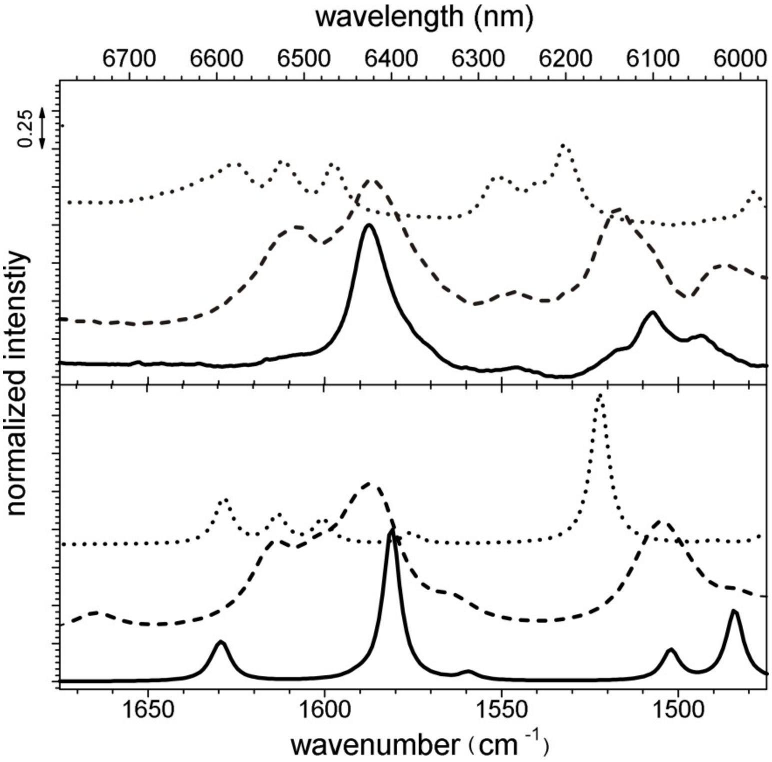

Fig. SI1a: Vibrational modes of 6MQz (solid), 6MQc (dotted) and intermediate (dashed)

top: Measured MIR spectra in acetonitrile

bottom: Calculated by B3LYP/6-311G**. 6MQz and 6MQc are calculated comprising the solvent polarity by SCRF, the intermediate structure is optimized involving dispersion forces with Grimme D3

Density Functional Theory

DFT calculations are carried out at the B3LYP/6-311G(d,p) level of theory. To reconstruct the measured IR pattern, SCRF correction was chosen for 6MQc and 6MQz. This correction has a large effect on the vibrational modes calculated for the ionic 6MQc but only minor effect on 6MQz. It was found that for 6MQz two water molecules are interacting with the negative oxygen via H-bonds. Working with such small dye concentrations this is unavoidable. Even very little moisture will provide 2 water molecules per one dye molecule. In case of cationic 6MQc we found a water mediated cation anion pair.

The intermediate structure is shown in Fig. SI1b. The two dye molecules share one proton via a hydronium ion like water molecule. The O-H distances show that there are no stationary conditions. The proton is dynamically fluctuating between both 6MQz oxygens. The anion interacts with both N heterocycles. The planar dye molecules are arranged with an angle of 41° towards each other.

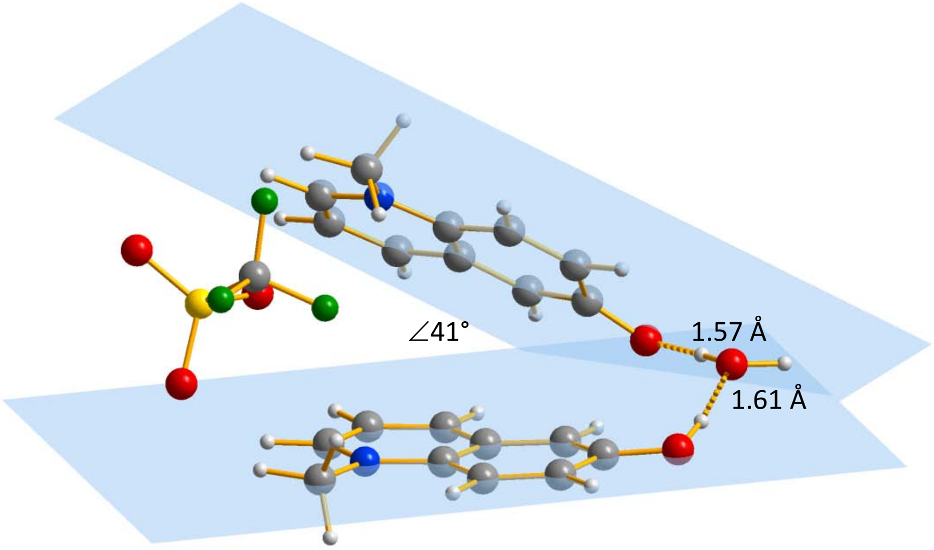

Fig. SI1b: Optimized geometry of intermediate calculated by DFT at the B3LYP/6-311G** level of theory. The structure and corresponding vibrations are calculated considering Grimme D3 dispersion.

SI2 UV-vis absorption spectra of pure species in acetonitrile delivered by decomposition of measured spectra

The UV-vis spectra of the three species in acetonitrile are calculated from the measured titration range. The spectra of pure 6MQz and 6MQc are given by the first and the last point of the titration and represent two of the three given linear independent spectra from Singular Value Decomposition. The absorption of the intermediate is extracted from the data range by fitting a sum of weighted 6MQz and 6MQc spectra to the data. Therefore, a·6MQz + b·6MQc is adapted to the data under two conditions: 1) the sum of the squares of deviations between the spectra is minimized 2) the maximal absorption is given by the measured spectra. The spectrum of the intermediate is received as difference between measured and fitted spectrum at each point of the titration. All calculated intermediate spectra show the same features.

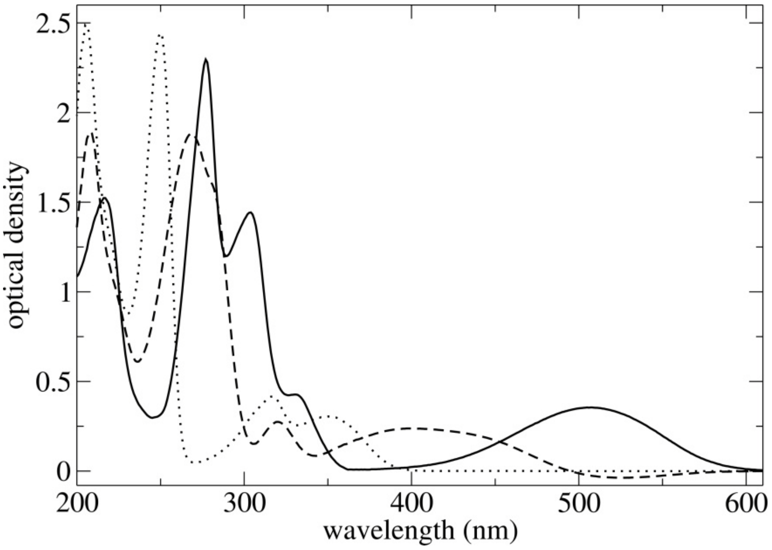

Fig. SI2: Absorption spectra of pure 6MQz (solid), intermediate (dashed) and 6MQc (dotted) in acetonitrile extracted from measured data range.

SI3 Quantitative analysis of acid base titration of 6MQz in imidazolium ILs

The zwitterionic dye 6MQz is protonated by adding trifluoromethanesulfonic acid stepwise. Dealing with a “one to one” reaction we make sure working with an acid concentration in the range of infinite dilution, as well as for the dye. Therefore, the activity coefficient for all species involved is set to one and the activities are equal to the concentrations.

As solvent two imidazolium ILs with different anions BF_4 and dicyanamide (DCA) are chosen. After each step of titration the UV-vis spectra are collected. The ranges of spectra are shown in Fig. SI3a.

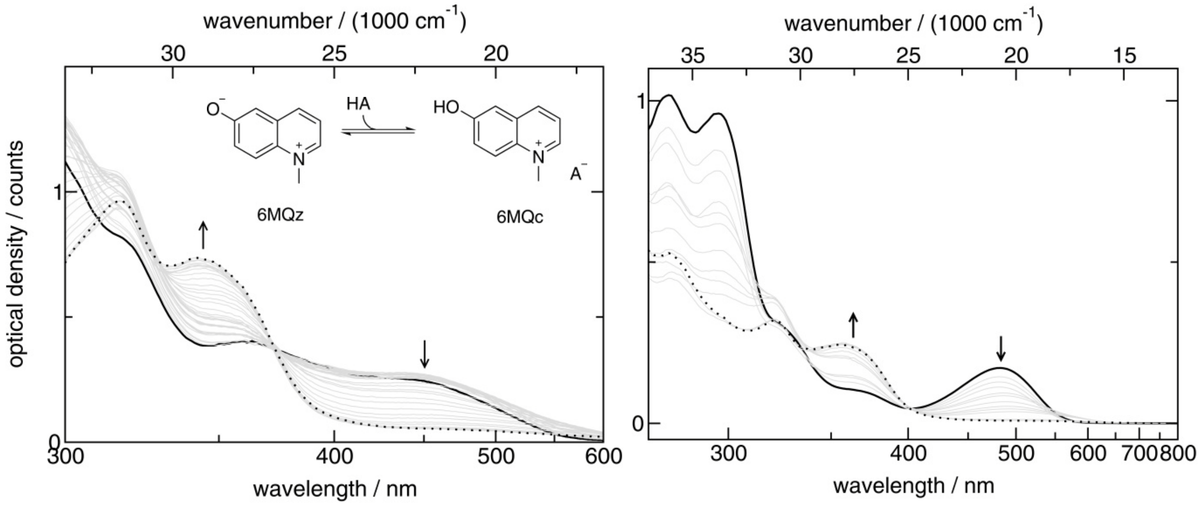

Fig. SI3a: UV-vis absorption spectra of the quinolinium dye with different protonation in $[C_4mim][BF_4]$ (left) and $[C_4mim][DCA]$ (right). The first spectrum is presented by the accentuated solid black line, the last spectrum by the dotted one. The chemical reaction is shown as well.

The spectra are decomposed by Singular Value Decomposition. Fitting Eq. 6-8 iteratively to the data results in the acid dissociation constants.

$$[\mathrm{MQz}] = \frac{\mathrm{K_a}[\mathrm{MQ}]_\mathrm{T}}{[\mathrm{H^+}] + \mathrm{K_a}} \qquad (\mathrm{Eq.}\,6)$$

$$[\mathrm{MQz}] = \frac{[\mathrm{MQ}]_\mathrm{T}[\mathrm{H^+}]}{[\mathrm{H^+}] + \mathrm{K_a}} \qquad (\mathrm{Eq.}\,7)$$

$$[\mathrm{H^+}] = \frac{1}{2}\Big(-[\mathrm{MQ}]_\mathrm{T} + [\mathrm{H}]_\mathrm{T} - \mathrm{K_a} + \sqrt{(-[\mathrm{MQ}]_\mathrm{T} + [\mathrm{H}]_\mathrm{T} - \mathrm{K_a})^2 + 4[\mathrm{H}]_\mathrm{T}\mathrm{K_a}}\Big) \qquad (\mathrm{Eq.}\,8)$$

The negative logarithm gives the pK_a values of 5.5 for $[C_4mim][BF_4]$ and 4.1 for $[C_4mim][DCA]$, respectively. The acid dependent species associated concentration profiles are shown in Fig. SI3b.

In $[C_4mim][BF_4]$ the expected behavior is observed. At the first spectrum solely the zwitterion 6MQz is present. At half equivalent acid ($[HA]=1.25\ 10^{-3}\ \mathrm{mol\ l^{-1}}$) half of the initial dye concentration ($[MQ]_T = 2.49\ 10^{-3}\ \mathrm{mol\ l^{-1}}$) is converted to the protonated form. When 1 eq. acid is added, the dye is completely protonated.

In $[C_4mim][DCA]$ we observe a different process. Just in the beginning, before adding any amount of acid, the zwitterion is partly protonated. From the plotted data a portion of $1.07\ 10^{-4}\ \mathrm{mol\ l^{-1}}$ 6MQc is calculated for the first measured spectrum. This equates to 27 % of the initial dye concentration of $3.97\ 10^{-4}\ \mathrm{mol\ l^{-1}}$.

Obviously, the dicyanamide acidifies the C_2-H of the imidazolium, what is transferred to the zwitterion.

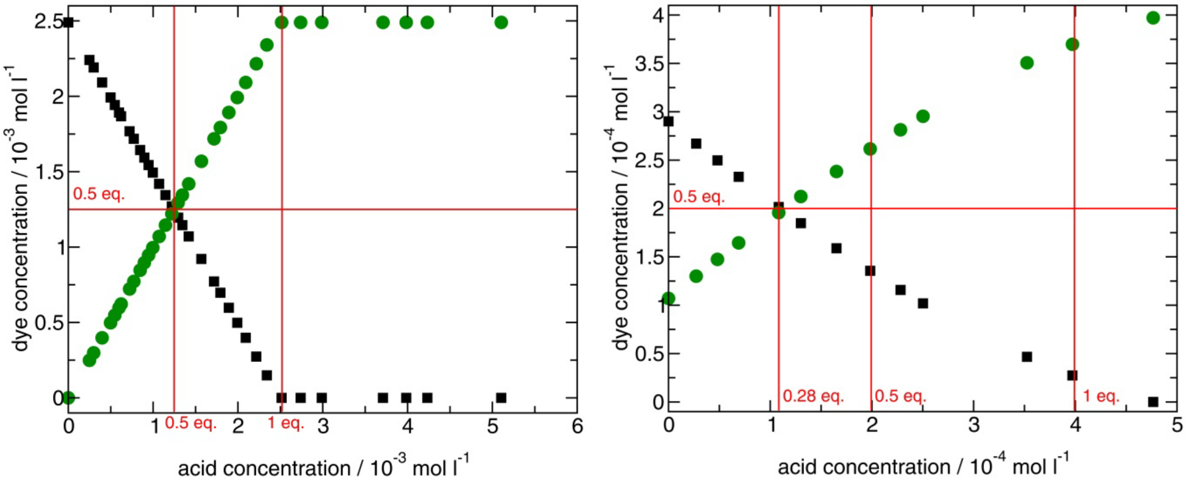

Fig. 3b: Concentration profiles for 6MQz (black) and 6MQc (green) calculated from the measured titration data in $[C_4mim][BF_4]$ (left) and $[C_4mim][DCA]$ (right). In the DCA IL there is already 6MQc formed at the first measured spectrum, wherein no acid is added to the reaction mixture.

SI4 Fluorescence in $[C_4mim][PF_6]$ and $[HPPy][NTf_2]$

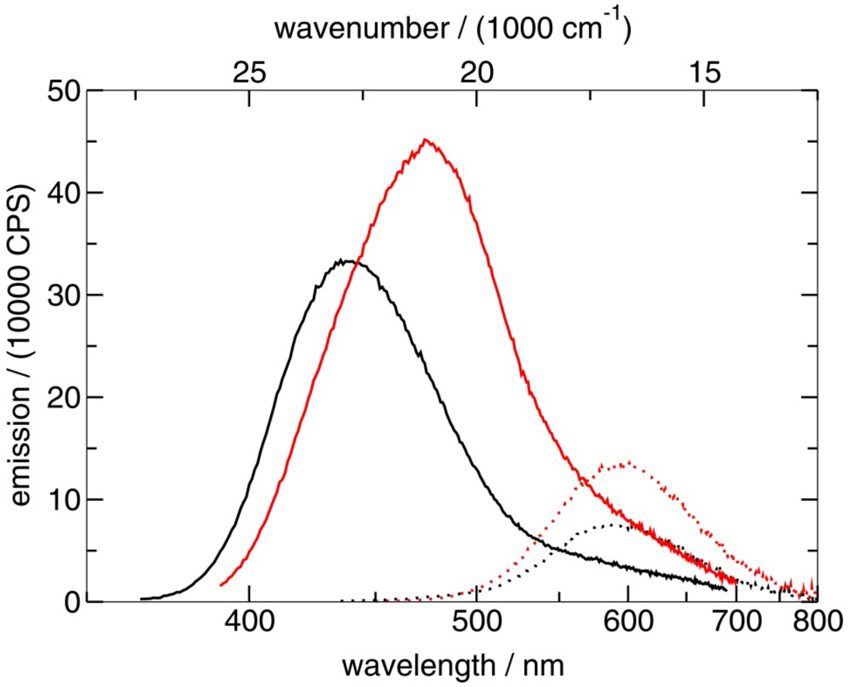

Fig. SI4: Fluorescence response of 6MQz in ILs of moderate acidity. $[C_4mim][PF_6]$ (black) and $[HPPy][NTf_2]$ (red) show emission of both forms. The zwitterion is excited at 420 nm and presented by the dotted lines, whereas a excitation wavelength of 350 nm gives the fluorescence response of the cationic 6MQc (solid line).