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Synthesis and Spectroscopic Characterization of 1,8-Naphthalimide Derived “Super” Photoacids

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Supporting Information

ABSTRACT: The ground- and excited-state acid–base properties of three novel naphthalimide-based “super” photoacids were studied using steady-state and time-resolved spectroscopy. The compounds exhibit $pK_a = 8.8–8.0$ and $pK_a^* = 1.2$ to $1.9$. The decrease in both ground- and excited-state $pK_a$ is achieved by attachment of an electron withdrawing group (sulfonate) on the aromatic system. All compounds are deprotonated upon excitation in alcohols and DMSO. Good correlation is established between the $pK_a$ and the ratio of the neutral and anion emission intensities in a certain solvent. The excited-state intermolecular proton transfer to solvent (H$_2$O and DMSO) is explained by a two-step model. In the first step, short-range proton transfer takes place, resulting in the formation of a contact ion pair. Free ion pairs are formed in the diffusion controlled second step.

INTRODUCTION

The acidity of many hydroxy-substituted aromatic compounds increases dramatically upon electronic excitation. Excitation of a neutral form of this class of molecules, known as photoacids, results in excited-state proton transfer (ESPT) to the solvent in aqueous solutions. This is manifested by dual emission from the neutral (ROH$^+$) and anionic (RO$^-*$) forms. After 60 years of its first description by Förster, excited-state proton-transfer (ESPT) reactions remain an active topic in biology and physical chemistry and the field has been reviewed several times.

Most well-known classes of photoacids are based on naphthols, hydroxyquinolines, and hydroxypyrenes. The photoacidity is generally explained by a partial intramolecular charge transfer from the hydroxyl oxygen to the aromatic ring in the excited state. Thus, introduction of electron withdrawing groups, such as cyano or sulfonate groups, on the aromatic system increases the acidity in both the ground and excited states.

While 2-naphthol has a $pK_a$ of 9.5 in the ground state and $pK_a^* = 2.8$ in the excited state, its cyano-functionalized derivatives exhibit $\Delta pK_a \approx -8$ to $-12$ units upon excitation and $pK_a^* \approx 0$ to $-4$ depending on the number and positions of the cyano groups. Tolbert et al. introduced the term “super” photoacids to describe these enhanced photoacids possessing negative $pK_a^*$ values and the ability to deprotonate in organic solvents, such as alcohols and dimethyl sulfoxide (DMSO), in the absence of water. Recently, Jung et al. used a similar approach to enhance the acidity of the well-known 8-hydroxypyrene-1,3,6-trisulfonate (HPTS, $pK_a \approx 7.4$ and $pK_a^* \approx 0.4$) photoacid. Substitution of the sulfonate groups by more electron withdrawing sulfonamide or sulfonic ester groups resulted in $pK_a^* = 5.7$–$4.4$ and $pK_a^* = -0.8$ to $-3.9$.

Substituted 1,8-naphthalimides are widely employed as probes and sensors due to their fluorescent properties. The naphthalimide (NI) skeleton offers a flexible and robust template in which both aromatic and $N$-substitution are easily accessible. Hydroxy-substitution of the aromatic system has been shown to introduce photoacidic properties resulting in dual fluorescence. Biczók et al. studied fluorescence quenching and intermolecular ion pair formation of 3- and 4-hydroxy-N-methyl-1,8-naphthalimides, but the studies were done solely in organic solvents. To the best of our knowledge, no studies on excited-state acid–base reactions of hydroxy-1,8-naphthalimides in aqueous solutions have yet been reported.

We present now the syntheses and photophysical characterizations of three novel NI-derived photoacids (Scheme 1). First, we will report steady-state characterization of all three compounds in water and organic solvents. Second, we will show ps time-resolved fluorescence (time-correlated single photon counting, TCSPC) studies of all compounds in DMSO. Third, we will report a more thorough investigation of a selected photoacid, EG-dHONI, in aqueous solutions including ps time-resolved fluorescence and ns transient absorption (flash photolysis). We will also evaluate the possibility of dianion formation (deprotonation of both hydroxyl groups) by means of steady-state electronic and NMR spectroscopies. Last, we will show results of quantum chemical calculations (DFT and TD-DFT) to gain more insight into the effect of substitution on the photoacidic and spectroscopic properties.

The results are analyzed within the already established framework of ground- and excited-state acid–base reactions. Briefly, the overall deprotonation process will be explained by a...
two-step model (Scheme 2) originally proposed by Eigen and Weller.6,32 In the model, the initial short-range proton transfer results in formation of a contact ion pair followed by diffusion controlled separation of the ions.15,33,34 Different decay pathways are also indicated in the scheme including a quenching process by protons. The decay of the ground-state anion, measured by flash photolysis, is analyzed using pseudo-first-order, mixture of first- and second-order, and pure second-order reaction kinetics at low, intermediate, and neutral pH, respectively.35,36

EXPERIMENTAL SECTION

Materials. The reaction scheme for the synthesis of the target compounds is depicted in Scheme 1. All three photoacids were synthesized starting from 1,8-naphthalic anhydride by sulfonation with fuming sulfuric acid to give sodium-1,8-naphthalic anhydride-3,6-disulfonate.37 The disulfonate was converted to either potassium-3-hydroxy-1,8-naphthalic anhydride-6-sulfonate or 3,6-dihydroxy-1,8-naphthalic anhydride by reaction with molten KOH at 200−250 °C. The main product was either the mono- or dihydroxy compound depending on the reaction time. Reaction with a primary amine (diethylene glycolamine or glycine methyl ester) yielded the corresponding 1,8-naphthalimides. Hydrolysis of the ester under basic conditions afforded the corresponding carboxylic acid. Detailed descriptions of the synthetic procedures and characterizations of the compounds are given in the Supporting Information. Other used materials are also described in the Supporting Information.

Spectroscopic Measurements. All NMR spectra were recorded using a Bruker Avance 400 or DRX 500 spectrometer. IR spectra were recorded using a Bruker Alpha-P spectrometer. Steady-state absorption and fluorescence spectra were recorded using a Shimadzu UV-2700 spectrophotometer and a SPEX Fluorolog3-22 fluorimeter, respectively. The fluorescence spectra were collected in a right-angle geometry and corrected for the spectral sensitivity of the instrument. All measurements were carried out at room temperature (21 ± 1 °C). The concentrations of the samples were 7−120 μM. Quantum yields were determined using quinine sulfate (>99%, Fluka) in 0.5 M H2SO4 (aq.) as a quantum yield standard with Φf = 0.55.38,39 Experimental setups for time-resolved (TCSPC and flash photolysis) and other (pH and Karl Fischer) measurements are described in the Supporting Information.

Theoretical Calculations. All calculations were performed with the ADF2013 software40,41 using the PBE0 functional42,43 and the TZ2P44 basis set. We chose the PBE0 functional because it has been shown to produce reasonable results for 1,8-naphthalimide dyes.45,46 The conductor-like screening model (COSMO)47 was used to include solvent effects for all DFT and TD-DFT calculations.

RESULTS

Steady-State Measurements in Aqueous Solutions. Ground-state pK:\textsubscript{a} values were determined by measuring absorption spectra over a broad pH range. Mild buffer solutions (c = 5−10 mM) were used for intermediate pH values (pH 3.0−10.5). Aqueous H2SO4 or NaOH were used for lower and higher pH ranges, respectively. The absorption spectra of EG-dHONI show a clear conversion from the neutral to the anionic form with an isosbestic point at λ = 402 nm. A second isosbestic point was observed at λ = 317 nm, but the last four spectra measured at the highest pH values deviated slightly from this point. The reason for the deviation is most likely minor hydrolysis (ring opening of the imide group) at high pH which will be discussed later. Interestingly, the absorption spectrum of EG-SHONI showed splitting of the main absorption band into two bands (see Figure 9). Both bands
were red-shifted upon conversion to the anionic form (Supporting Information).

Concentrations of the neutral and anionic forms were calculated using the Lambert–Beer law at two selected wavelengths close to the absorption maxima of the neutral \( \lambda_{\text{ROH}} \approx 380 \text{ nm} \) and anionic forms \( \lambda_{\text{RO}^-} \approx 440 \text{ nm} \). Ground-state pKₐ values were estimated from the midpoints of the molar fraction data. Absorption spectra of EG-dHONI at different pH values are presented in Figure 1. Absorption spectra of COOH-dHONI and EG-SHONI are shown in Figures S1 and S2, respectively (Supporting Information).

Excited-state pKₐ values were estimated using the Förster cycle. Absorption and emission spectra of the neutral form were measured in 2 M H₂SO₄ and aqueous NaOH (pH \( \approx 11–12 \)) for the spectra of the anionic form. Emission of the anion was measured upon direct excitation of the anion absorption band at \( \sim 440 \text{ nm} \). The emission spectra measured in 2 M H₂SO₄ still exhibited anion emission, but this should not significantly affect the emission maxima of the neutral band. The anion emission in this solvent was strongest for EG-SHONI and weakest for EG-dHONI. We used an average of absorption and emission maxima as the 0–0 transitions, \( \nu_{00} = (\nu_{\text{abs}}^{\max} + \nu_{\text{em}}^{\max})/2 \). Absorption and emission spectra of the neutral and anionic forms of EG-dHONI are presented in Figure 2. Spectra of COOH-dHONI and EG-SHONI are given in Figures S3 and S4, respectively (Supporting Information).

Absorption maxima and molar absorption coefficients of the neutral and anionic forms and ground- and excited-state pKₐ values are summarized in Table 1.

**Fluorescence Spectra and Quantum Yields in H₂O and Organic Solvents.** Excited-state deprotonation in water and protic and aprotic organic solvents was studied by means of steady-state fluorescence spectroscopy. Emission spectra and quantum yields \((\Phi_i)\) were measured in H₂O, MeOH, EtOH, 2-ProOH, n-BuOH, and DMSO. The emission spectra were fitted with a sum of skewed gaussians (eq 1) to decompose the quantum yields for neutral and anionic forms. Two skewed gaussians were sufficient to adequately model the emission spectra in water and alcohols, whereas a sum of three skewed gaussians was required for samples in DMSO.

\[
I(\lambda) = Y \left\{ \exp\left[\ln(2) \frac{\ln(1 + a/b)^2}{2} \right] \right\} \begin{cases} 1 & \alpha > -1 \\ 0 & \alpha \leq -1 \end{cases}
\]

In eqs 1 and 2, \( Y \) is the peak intensity, \( x_0 \) the peak position, \( \Delta x \) the bandwidth, and \( b \) the asymmetry parameter. Normalized emission spectra of EG-dHONI in organic solvents are presented in Figure 3. The spectra of COOH-dHONI and EG-SHONI are given in Figures S5 and S6, respectively (Supporting Information). The spectrum in water (Figure S7, Supporting Information) is left out to allow better comparison between the spectra in organic solvents. Representative fits of the emission spectra of EG-dHONI in DMSO with a sum of two or three skewed gaussians are given in Figures S8 and S9, respectively (Supporting Information).

Following the analogy presented by Jung et al., the ratio \( \Phi_{\text{ROH}}/\Phi_{\text{RO}^-} \) follows the same trend as the pKₐ and reflects the efficiency of deprotonation. The assumption should be valid for a set of similar compounds with similar fluorescence lifetimes and quantum yields in a certain solvent. The ratios for all three compounds in different solvents are presented in Figure 4. The total quantum yields, fraction of total emission attributed to ROH*, and ratios of the neutral and anion fluorescence quantum yields are summarized in Table 2.

Fluorescence quantum yields in water were dependent on pH but were \( \Phi_i < 0.5\% \) in all cases. Quantum yields increased from 2 M H₂SO₄ to pH 3 but remained constant at pH 3–7. Also, the ratio \( \Phi_{\text{ROH}}/\Phi_{\text{RO}^-} \) was dependent on the pH but did not change significantly at pH 3–7 upon excitation of the neutral form. Normalized emission spectra of EG-dHONI at different pH values are shown in Figure S7 (Supporting Information).

**Time-Resolved Fluorescence in DMSO.** Deprotonation kinetics of all compounds were studied in DMSO with the TCSPC method. Samples were found to be unstable in the presence of oxygen upon laser irradiation and were thus deoxygenated by argon bubbling. The decay of the neutral form was monitored with \( \lambda_{\text{mon}} = 430 \text{ nm} \) with a 10 ns time window and fitted with a three-exponential model (eq S1 with \( n = 3 \), Supporting Information). The decay of the anion was monitored with \( \lambda_{\text{mon}} = 610 \text{ nm} \) with a 50 ns time window and fitted with a two-exponential model (eq S1 with \( n = 2 \), Supporting Information). Decays of EG-dHONI together with the instrument response function are presented in Figure 5, and decays of COOH-dHONI and EG-SHONI are shown in

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**Figure 1.** Absorption spectra of EG-dHONI \((c = 30 \text{ µM})\) at different pH values. The inset shows the molar fractions of the neutral and anionic forms as a function of pH.

**Figure 2.** Normalized absorption and emission spectra of the neutral and anionic forms of EG-dHONI in aqueous solutions.
Figures S10 and S11, respectively (Supporting Information). All the fitting results are summarized in Table 3. All compounds exhibited a fast component ($\tau_1 < 25$ ps = IRF) at the neutral band. The component with the largest amplitude had a lifetime of $\tau_2 = 620 - 860$ ps. The rise of the anion emission at 610 nm showed a similar lifetime but seemed somewhat faster. Also, the amplitude associated with the rise time was only $\sim 50\%$ of the total amplitude of the positive component. In addition, the neutral region exhibited a longer-lived tail with a small amplitude ($\alpha_3 < 4\%$). The anion emission showed long-lived decay with a lifetime of $\tau_2 = 14.6 - 16.7$ ns.

All decay traces were well described by the multiexponential model and $\chi^2 < 1.13$ in all cases.

Time-Resolved Fluorescence of EG-dHONI in Aqueous Solutions at Different pH Values. Excitation of EG-dHONI in acidic aqueous solutions led to emission of the neutral and anionic forms, which were monitored at $\lambda_{\text{mon}} = 420 - 480$ nm and $\lambda_{\text{mon}} \approx 530 - 630$ nm, respectively. In this case, the samples were photostable and deoxygenation was unnecessary. The decay traces were fitted with three- (in 0.5 M H$_2$SO$_4$) or four-exponential (pH 3.0, 4.8, and 6.5) models with global lifetimes (eq S1 with $n = 3$ or 4, Supporting Information).

Representative decay associated spectra (DAS) at pH 4.8 are presented in Figure 6. The DAS in 0.5 M H$_2$SO$_4$ and at pH 3.0 and 6.5 are shown in Figures S12–S14 (Supporting Information). Individual decay traces at selected wavelengths for all samples are shown in Figures S15–S18 (Supporting Information). The fitting results are summarized in Table 4. All DAS exhibited a fast component with $\tau_1 < 25$ ps as the main decay component in the neutral region. The same component also appeared as a rise time in the anion spectral range. In addition, all spectra showed an intermediate component. In addition, the neutral region exhibited a longer-lived tail with a small amplitude ($\tau_2 < 4\%$). The anion emission showed long-lived decay with a lifetime of $\tau_2 = 14.6 - 16.7$ ns. All decay traces were well described by the multieponential model and $\chi^2 < 1.13$ in all cases.

Time-Resolved Fluorescence of EG-dHONI in Aqueous Solutions at Different pH Values. Excitation of EG-dHONI in acidic aqueous solutions led to emission of the neutral and anionic forms, which were monitored at $\lambda_{\text{mon}} = 420 - 480$ nm and $\lambda_{\text{mon}} \approx 530 - 630$ nm, respectively. In this case, the samples were photostable and deoxygenation was unnecessary. The decay traces were fitted with three- (in 0.5 M H$_2$SO$_4$) or four-exponential (pH 3.0, 4.8, and 6.5) models with global lifetimes (eq S1 with $n = 3$ or 4, Supporting Information). Representative decay associated spectra (DAS) at pH 4.8 are presented in Figure 6. The DAS in 0.5 M H$_2$SO$_4$ and at pH 3.0 and 6.5 are shown in Figures S12–S14 (Supporting Information). Individual decay traces at selected wavelengths for all samples are shown in Figures S15–S18 (Supporting Information). The fitting results are summarized in Table 4. All DAS exhibited a fast component with $\tau_1 < 25$ ps as the main decay component in the neutral region. The same component also appeared as a rise time in the anion spectral range. In addition, all spectra showed an intermediate component. In addition, the neutral region exhibited a longer-lived tail with a small amplitude ($\tau_2 < 4\%$). The anion emission showed long-lived decay with a lifetime of $\tau_2 = 14.6 - 16.7$ ns. All decay traces were well described by the multieponential model and $\chi^2 < 1.13$ in all cases.

Table 1. Absorption Maxima and Molar Absorption Coefficients of the Neutral and Anionic Forms and Ground- and Excited-State $pK_a$ Values

<table>
<thead>
<tr>
<th>compound</th>
<th>$\lambda_{\text{ROH}}^{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{ROH}}^{\text{max}}$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{RO}}^{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{RO}}^{\text{max}}$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$pK_a$</th>
<th>$pK_a^*$</th>
<th>$\Delta pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG-dHONI</td>
<td>381</td>
<td>11000 ± 300</td>
<td>440</td>
<td>10400 ± 400</td>
<td>8.8 ± 0.1</td>
<td>-1.2</td>
<td>-10.0</td>
</tr>
<tr>
<td>COOH-dHONI</td>
<td>382</td>
<td>11300 ± 400</td>
<td>439</td>
<td>10300 ± 400</td>
<td>8.8 ± 0.1</td>
<td>-1.4</td>
<td>-10.3</td>
</tr>
<tr>
<td>EG-SHONI</td>
<td>384</td>
<td>6100 ± 200</td>
<td>444</td>
<td>5000 ± 200</td>
<td>8.0 ± 0.1</td>
<td>-1.9</td>
<td>-9.9</td>
</tr>
</tbody>
</table>

Table 2. Total Quantum Yields ($\Phi_f$), Fraction of Total Emission Attributed to ROH* ($\alpha_{\text{ROH}}$), and Ratios of the Neutral and Anion Fluorescence Quantum Yields of the Studied Compounds in a Series of Solvents

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\Phi_f$</th>
<th>$\alpha_{\text{ROH}}$</th>
<th>$\Phi_{\text{ROH}}/\Phi_{\text{RO}}$</th>
<th>$\Phi_f$</th>
<th>$\alpha_{\text{ROH}}$</th>
<th>$\Phi_{\text{ROH}}/\Phi_{\text{RO}}$</th>
<th>$\Phi_f$</th>
<th>$\alpha_{\text{ROH}}$</th>
<th>$\Phi_{\text{ROH}}/\Phi_{\text{RO}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>&lt;0.005</td>
<td>4.8%</td>
<td>0.05</td>
<td>&lt;0.005</td>
<td>4.6%</td>
<td>0.05</td>
<td>&lt;0.005</td>
<td>3.6%</td>
<td>0.04</td>
</tr>
<tr>
<td>DMSO</td>
<td>0.17</td>
<td>30%</td>
<td>0.43</td>
<td>0.17</td>
<td>26%</td>
<td>0.36</td>
<td>0.17</td>
<td>22%</td>
<td>0.38</td>
</tr>
<tr>
<td>MeOH</td>
<td>0.01</td>
<td>73%</td>
<td>2.70</td>
<td>0.02</td>
<td>72%</td>
<td>2.61</td>
<td>0.01</td>
<td>51%</td>
<td>1.05</td>
</tr>
<tr>
<td>EtOH</td>
<td>0.03</td>
<td>85%</td>
<td>5.49</td>
<td>0.03</td>
<td>80%</td>
<td>3.93</td>
<td>0.03</td>
<td>67%</td>
<td>2.04</td>
</tr>
<tr>
<td>2-PrOH</td>
<td>0.06</td>
<td>92%</td>
<td>11.7</td>
<td>0.05</td>
<td>90%</td>
<td>9.45</td>
<td>0.06</td>
<td>80%</td>
<td>4.00</td>
</tr>
<tr>
<td>n-BuOH</td>
<td>0.06</td>
<td>93%</td>
<td>13.5</td>
<td>0.05</td>
<td>89%</td>
<td>7.82</td>
<td>0.06</td>
<td>84%</td>
<td>5.40</td>
</tr>
</tbody>
</table>
Di showed induced absorption with excitation ($\lambda_{\text{abs}}$ absorption) at pH 3.0, 5.0, and 7.0 was studied by nanosecond transient and will be discussed later. The fast component (faster than IRF) and the long-lived tail, intermediate component with quantum yields in this pH range, and exhibited a third component with only in the emission range of the anion. The DAS at pH 3.0 showed the emission of the anion band. The spectra also showed the emission of the anion was calculated on the basis of the molar absorption coefficient (see Table 1).

![Figure 6. Decay associated spectra of EG-dHONI at pH 4.8. The excitation wavelength was 380 nm. The inset shows the individual $\chi^2$ values.](image)

| Table 3. Decay Times $\tau$ and Amplitudes $\alpha$ of the Decays of All Photoacids in DMSO |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| compound                      | neutral ($\lambda_{\text{max}} = 430 \text{ nm}$) | anion ($\lambda_{\text{max}} = 610 \text{ nm}$) |
| $\tau_1$ ($\alpha_1$) (ps)    | $\tau_2$ ($\alpha_2$) (ps) | $\tau_3$ ($\alpha_3$) (ns) | $\chi^2$ | $\tau_1$ ($\alpha_1$) (ps) | $\tau_2$ ($\alpha_2$) (ps) | $\chi^2$ |
| EG-dHONI                      | 25 (22%)         | 860 ± 40 (74%)   | 1.6 ± 0.1 (4%) | 1.04 | 650 ± 80 (43%) | 14.7 ± 0.1 (100%) | 1.09 |
| COOH-dHONI                    | 25 (37%)         | 740 ± 30 (60%)   | 1.8 ± 0.2 (3%) | 1.08 | 540 ± 80 (47%) | 14.6 ± 0.1 (100%) | 1.03 |
| EG-SHONI                      | 25 (17%)         | 620 ± 20 (82%)   | 3.4 ± 0.4 (1%) | 1.13 | 450 ± 60 (62%) | 16.7 ± 0.2 (100%) | 1.02 |

Component with $\tau_1$ ≈ 75 ps. In 0.5 M H$_2$SO$_4$, this component had positive amplitude in both the neutral and anion bands, whereas at pH 3.0–6.5 the component had positive amplitude only in the emission range of the anion. The DAS at pH 3.0–6.5 were almost identical, as expected based on the equal quantum yields in this pH range, and exhibited a third intermediate component with $\tau_3 = 470$ ps. All spectra showed a longer-lived tail with very small amplitude (<1%) throughout the whole wavelength range. The decay traces were very well described by the multieponential model in the anion wavelength range in all cases. The $\chi^2$ values were less satisfactory (~1.2–1.3) in the neutral region. This was due to the fast component (faster than IRF) and the long-lived tail, which was not that well described by the exponential function and will be discussed later.

Decays of the Ground-State Anion of EG-dHONI at Different pH Values. The decay of the ground-state anion formed after excited-state deprotonation at different pH values (pH 3.0, 5.0, and 7.0) was studied by nanosecond transient absorption (flash photolysis). Samples were deoxygenated by argon bubbling to avoid photodegradation under intense laser excitation ($E = 1.5–2.5$ mJ/pulse). The transient spectra showed induced absorption with $\lambda_{\text{max}} = 440$ nm corresponding to the anion band. The spectra also showed the emission of the anion in the first trace at $t = 0$ ns. The transient spectra are shown in Figures S19–S21 (Supporting Information). Decay traces were obtained by averaging the signal at $\lambda = 438–442$ nm and are presented in Figure 7. The excitation wavelength was 440 nm at different pH values. The concentration of the anion was calculated on the basis of the molar absorption coefficient (see Table 1).

![Figure 7. Decays of the ground-state anion monitored at 440 nm at different pH values. The excitation wavelength was 380 nm.](image)

The decay at pH 3.0 was fitted with a single-exponential function (pseudo-first-order reaction). At intermediate pH 5.0 ($([\text{H}^+]_i \approx [\text{H}^+]_{\text{jump}}$), the decay was modeled with a function derived by Huppert et al. for recombination at intermediate pH values (eq 17 in ref 36). The model consists of a mixture of first- and second-order terms, and the initial proton concentration, $[\text{H}^+]_i$, is used as a fitting parameter. The decay at pH 7.0 is modeled as pure second-order bimolecular recombination. The fitting results are summarized in Table 5. The decays are very well described by the chosen models.

| Table 4. Global Lifetimes and $\chi^2$ Values of the Fittings of EG-dHONI in Aqueous Solutions at Different pH Values |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| solvent                        | $\tau_1$ (ps)   | $\tau_2$ (ps)   | $\tau_3$ (ps)   | $\tau_4$ (ns)   | $\chi^2$        |
| 0.5 M H$_2$SO$_4$               | 25              | 72 ± 2          | 1.7 ± 0.3       | 1.15            |
| pH 3.0                         | <25             | 74 ± 17         | 470 ± 10        | 3.6 ± 0.4       | 1.14            |
| pH 4.8                         | <25             | 72 ± 22         | 470 ± 10        | 2.4 ± 0.6       | 1.16            |
| pH 6.5                         | <25             | 80 ± 24         | 470 ± 10        | 2.0 ± 0.4       | 1.15            |

Decays of the Ground-State Anion of EG-dHONI at Different pH Values. The decay of the ground-state anion formed after excited-state deprotonation at different pH values (pH 3.0, 5.0, and 7.0) was studied by nanosecond transient absorption (flash photolysis). Samples were deoxygenated by argon bubbling to avoid photodegradation under intense laser excitation ($E = 1.5–2.5$ mJ/pulse). The transient spectra showed induced absorption with $\lambda_{\text{max}} = 440$ nm corresponding to the anion band. The spectra also showed the emission of the anion in the first trace at $t = 0$ ns. The transient spectra are shown in Figures S19–S21 (Supporting Information). Decay traces were obtained by averaging the signal at $\lambda = 438–442$ nm and are presented in Figure 7. The excitation wavelength was 440 nm at different pH values. The concentration of the anion was calculated on the basis of the molar absorption coefficient (see Table 1).

| Table 5. Fitting Results of the Decays of the Ground-State Anion of EG-dHONI at Different pH Values |
|---------------------------------|-----------------|-----------------|
| pH                             | $r^2$ (ns)      | $k_{\text{uni}}^F$ (x10$^{11}$ M$^{-1}$ s$^{-1}$) |
| 3.0                            | 23 ± 2          | 1.8 ± 0.1       |
| 5.0                            | 1.9 ± 0.1       |
| 7.0                            | 1.9 ± 0.1       |

"From single-exponential function. $b$Bimolecular recombination rate."

Possibility of the Formation of the Dianion of EG-dHONI. The possibility of deprotonating both hydroxyl groups of EG-dHONI under basic conditions was studied with UV−vis and NMR spectroscopy. The absorption spectrum showed time-dependent conversion of the anion absorption to a shorter-wavelength absorbing species ($\lambda_{\text{max}} = 354$ nm) in 1 M NaOH with isosbestic points at $\lambda = 311$ and 376 nm. The fully converted sample still showed a residual absorption band at ~440 nm. The rate of the conversion was obtained by fitting the absorption of the anion (at 440 nm) vs time with a seventh order polynomial function and taking the first derivative of the fit. The so-called graphical rate equation is obtained by plotting the derivative (i.e., rate) as a function of the absorption (i.e.,

![Figure 7. Decays of the ground-state anion monitored at 440 nm at different pH values. The excitation wavelength was 380 nm.](image)
The reversibility of the observed changes was studied by acidification of the sample after complete conversion. Gradual acidification revealed multiple absorbing species at intermediate pH values (pH 4–10) eventually (at pH < 2) resulting in an absorption spectrum of the neutral form with 3 nm blue shift (compared to the original absorption) and slightly increased absorption in the UV region (results not shown). The final product after acidification was concluded to be 3,6-dihydroxy-1,8-naphthalic anhydride confirmed by reference UV–vis measurements. Moreover, 1H NMR experiments showed that the naphthalimide undergoes a ring opening reaction under strongly basic conditions, forming a deprotonated carboxylic acid and amide groups. The amide group was cleaved upon acidification, and eventually, a ring closing reaction took place to form the anhydride under strongly acidic conditions (results not shown). Different forms of the naphthalimide and naphthalic anhydride as a function of pH together with the absorption maxima are shown in Scheme S1 (Supporting Information).

Quantum Chemical Calculations on Model Compounds. We used quantum chemical calculations to study the nature of the excited state resulting in photoacidity and to compare the effect of substitution. This was done by looking at the frontier orbitals and by comparing the Mulliken charges on the hydroxyl oxygen between optimized ground and excited states. All compounds showed diminished electron density on the hydroxyl oxygen in the frontier orbitals and by comparing the Mulliken charges on the hydroxyl oxygen between the optimized ground and excited states, respectively. In addition, we used TD-DFT to calculate the absorption and emission spectra of the model compounds.

The absorption spectra of the conversion are presented in Figure 8, and the graphical rate equation is shown in the inset together with a linear fit.

![Figure 8](image.png)

**Figure 8.** Absorption spectra of EG-dHONI in 1 M NaOH as a function of time. The inset shows the graphical rate equation of the conversion.

The frontier orbitals of dHONI are presented in Figure 10, and those of SHONI, 5CNHONI, and 6CNHONI are shown in Figures S22–S24, respectively (Supporting Information). The frontier orbitals showed diminished electron density on the hydroxyl oxygen in the first excited state (HOMO → LUMO) in all cases. This was also quantified by comparing the Mulliken charges of the hydroxyl oxygen in the optimized ground and excited states. All compounds showed decreased negative charge on the hydroxyl oxygen in the excited state. The magnitude of the change was relatively small and showed the trend SHONI < dHONI < 5CNHONI < 6CNHONI. Similar trends were also observed in corresponding C–O and O–H distances, but the differences were small (results not shown). All the parameters are summarized in Table 6.

**DISCUSSION**

Steady-State Measurements in Aqueous Solutions. EG-dHONI and COOH-dHONI exhibit their main absorption bands at ~380 nm with equal molar absorption coefficients. EG-SHONI exhibits two main bands, lower and higher in energy, with molar absorption coefficients roughly half of those observed for the dihydroxy compounds. The main absorption bands were shown to originate from HOMO–1 and HOMO to LUMO transitions. In EG-dHONI and COOH-dHONI, the two bands are merged to a single broad absorption, resulting in functionalized compounds, the splitting of the two bands was greater compared to dHONI (~0.6 eV vs ~0.1 eV). In the experimental spectra, the two bands of EG-SHONI are clearly separated, whereas EG-dHONI exhibits only a single main band with a small shoulder/broadening at shorter wavelength. The calculated and experimental absorption spectra of dHONI and SHONI are presented in Figure 9.

![Figure 9](image.png)

**Figure 9.** Calculated (for N-methyl-) and experimental (for N-EG-) absorption spectra of the neutral forms of dHONI and SHONI.

The reversibility of the observed changes was studied by acidification of the sample after complete conversion. Gradual acidification revealed multiple absorbing species at intermediate pH values (pH 4–10) eventually (at pH < 2) resulting in an absorption spectrum of the neutral form with 3 nm blue shift (compared to the original absorption) and slightly increased absorption in the UV region (results not shown). The final product after acidification was concluded to be 3,6-dihydroxy-1,8-naphthalic anhydride confirmed by reference UV–vis measurements. Moreover, 1H NMR experiments showed that the naphthalimide undergoes a ring opening reaction under strongly basic conditions, forming a deprotonated carboxylic acid and amide groups. The amide group was cleaved upon acidification, and eventually, a ring closing reaction took place to form the anhydride under strongly acidic conditions (results not shown). Different forms of the naphthalimide and naphthalic anhydride as a function of pH together with the absorption maxima are shown in Scheme S1 (Supporting Information).

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All calculations showed that the two lowest-energy absorption bands originate from π → π* transitions from HOMO–1 and HOMO to LUMO. In sulfonate- and cyano-functionalized compounds, the splitting of the two bands was greater compared to dHONI (~0.6 eV vs ~0.1 eV). In the experimental spectra, the two bands of EG-SHONI are clearly separated, whereas EG-dHONI exhibits only a single main band with a small shoulder/broadening at shorter wavelength. The calculated and experimental absorption spectra of dHONI and SHONI are presented in Figure 9.

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roughly a 2 times higher absorption coefficient compared to EG-SHONI. The anion bands show ~60 nm red shifts compared to those of the neutral compounds in all molecules. Emission spectra of all compounds show nearly mirror-image emission bands in the wavenumber domain, but the anionic form exhibits a substantially larger Stokes shift (~4600 cm⁻¹ vs ~7000 cm⁻¹ for EG-dHONI).

The ground-state pKₐ is not affected by N-substitution, whereas the aromatic sulfonate substituent decreases the pKₐ by 0.8 units. The excited-state pKₐ is affected both by N- and aromatic substitution, but the changes are relatively small (0.7 pKₐ units). The main reason for the lower pKₐ* of EG-SHONI is the decreased ground-state pKₐ. Actually, EG-SHONI exhibits the smallest ΔpKₐ upon excitation. The pKₐ*’s follow the trend EG-SHONI < COOH-dHONI < EG-dHONI, also supported by the ratios of the neutral and anion emission intensities in 2 M H₂SO₄.

Fluorescence Spectra and Quantum Yields in H₂O and Organic Solvents. The fluorescence quantum yields (Table 2) of all compounds are very low in H₂O (<0.5%) and alcohols (≤6%). This can be attributed to proton quenching. After ESPT, the proton recombination results in efficient deactivation of the excited state which is enhanced in more proton rich solvents such as water or methanol. Another quenching mechanism, reported for 1-naphthol, is protonation of the aromatic ring system in the excited state. Indeed, we observed deuteration of the H₁ and H₄ for EG-dHONI and COOH-dHONI and H₄ for EG-SHONI under basic conditions upon heating in D₂O in our NMR-experiments, but we could not reproduce this exchange photochemically (results not shown) under similar conditions (pH 3, UV-irradiation) as reported for 1-naphthol. Therefore, the protonation of the ring system does not play a role in the excited-state processes of the present compounds. Protonation of the carbonyl group could also be a possible quenching mechanism, but it would be difficult to separate experimentally from the other proton quenching mechanisms. In aprotic solvents, such as DMSO, the fluorescence quantum yield is significantly higher (17%).

The ratios of the neutral and anion fluorescence quantum yields of the studied compounds correlate with the pKₐ*’s in all studied solvents. Although the ratio in a certain solvent allows comparison between similar compounds, it does not necessarily reflect the absolute value of pKₐ* due to differences in quantum yields and lifetimes of the neutral and anionic forms in different solvents. Similarly, the percentage of the neutral emission reflects the amount of deprotonation and thus the pKₐ*.

Interestingly, the sum of two skewed gaussians was adequate to describe the emission spectra in aprotic solvents, whereas three were required for samples in DMSO. This is attributed to the much higher concentration of the intermediate proton-transfer species, the contact ion pair, as will be discussed below.

Time-Resolved Fluorescence in DMSO. The decays in DMSO (Table 3) can be explained by a two-step deprotonation process (Scheme 2). This gives rise to a two-exponential decay in the neutral region. The fastest component (τ₁ < 25 ps) in all cases corresponds to the initial relaxation to the equilibrium between the neutral form and the contact ion pair. The lifetime reflects the sum of the forward (kₑₑ) and backward (kₑ₋) rates of the initial step but is too fast (<IRF) for quantitative analysis of the rate constants. The second component (τ₂ = 620–860 ps) is the decay of the equilibrium state resulting in formation of the free ion pairs. This component has the largest amplitude in the neutral region, indicating that the equilibrium state has a significant population of the neutral form. The decay of the equilibrium state correlates with pKₐ*, i.e., is fastest for the strongest excited-state acid (EG-SHONI). This is most likely the result of a lower energy barrier for the diffusion controlled proton dissociation. Attachment of electron withdrawing groups on the aromatic system will increase the extent of intramolecular charge transfer (and acidity), leaving the oxygen less negatively charged. Thus, the Coulombic barrier for the escape of the proton is lowered, resulting in faster decay of the intermediate contact ion pair. The long-lived tail (τ₃ = 1.6–3.4 ns) with minor amplitude originates most likely from the geminate proton recombination, although this largely results in fluorescence quenching at least in protic solvents. Another possibility is minor impurities due to photo-degradation processes.

The rise times of the anion emissions show a similar trend as the decays of the equilibrium state but are ~200 ps shorter than the decays observed in the neutral region. Moreover, the

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Table 6. Calculated and Experimental Absorption and Emission Energies (in eV) and Changes in the Mulliken Charges on the Hydroxyl Oxygen upon Excitation

<table>
<thead>
<tr>
<th>compound</th>
<th>E_abs</th>
<th>E_fl</th>
<th>E_calc</th>
<th>E_em</th>
<th>E_em*</th>
<th>E_em-0</th>
<th>Δp(0)_{H₂O-GS}</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHONI</td>
<td>3.28</td>
<td>3.23</td>
<td>3.02</td>
<td>2.66</td>
<td>3.15</td>
<td>b</td>
<td>2.94</td>
</tr>
<tr>
<td>dHONI</td>
<td>3.25</td>
<td>3.26</td>
<td>2.94</td>
<td>2.68</td>
<td>3.09</td>
<td>b</td>
<td>2.97</td>
</tr>
<tr>
<td>5CNHONI</td>
<td>3.08</td>
<td>a</td>
<td>2.71</td>
<td>a</td>
<td>2.89</td>
<td>b</td>
<td>a</td>
</tr>
<tr>
<td>6CNHONI</td>
<td>3.22</td>
<td>a</td>
<td>2.88</td>
<td>a</td>
<td>3.05</td>
<td>b</td>
<td>a</td>
</tr>
</tbody>
</table>

*Experimental data not available. **Average of absorption and emission maxima. Change in Mulliken charge of the hydroxyl oxygen.
negative amplitudes are only half of the positive counterparts. This can be partly attributed to the large overlap between the emission of the contact ion pair and the free ion pair at the monitoring wavelength (610 nm). In the spectral-line-shape analysis of EG-dHONI, the intermediate emission band centered at ~636 nm can be attributed to the contact ion pair (Figure S9, Supporting Information) and has ~20% intensity of the major emission band attributed to the free ion pair. This would result in observation of roughly ~80% negative amplitude in the time-resolved experiments at this monitoring wavelength. This means that part of the anions are formed directly during the IRF and only part via the intermediate state, namely, the contact ion pair. The disagreement between the lifetimes of the intermediate component could arise from the poorly resolved initial decay mixed with the intermediate component especially in the anion spectral range. The long-lived component ($\tau_2 = 14.6-16.7$ ns) in the anion emission band corresponds to the decay of the anion.

A more sophisticated three-step deprotonation model has been proposed by Huppert et al.33,37 and also discussed by us in a previous publication58 which could explain the disagreement between the lifetimes and amplitudes of the rise and decay components. In this model, an additional species, namely, the solvent separated ion pair, is introduced, which results in an additional decay component. Thus, the anion spectral range should be fitted with a four-exponential model (initial relaxation to equilibrium, contact ion pair, solvent separated ion pair, and free ion pair). Our data, however, were adequately fitted already with the two-exponential model. In addition, the best spectral fittings were achieved already with three spectral-line-shape functions supporting the two-step deprotonation model. More thorough measurements over a wider wavelength range would be required for full spectral and kinetic separation of all the overlapping components and is out of the scope of the present study.

**Time-Resolved Fluorescence of EG-dHONI in Aqueous Solutions at Different pH Values.** The decays of EG-dHONI in aqueous solutions (Table 4) can also be modeled by the two-step deprotonation mechanism. Similarly to results in DMSO, the ultrafast component ($\tau_1 < 25$ ps) corresponds to the initial relaxation of the neutral form to equilibrium between the contact ion pair followed by decay of the equilibrium state ($\tau_2 \approx 75$ ps). In 0.5 M H$_2$SO$_4$, the equilibrium state has a minor population of the neutral form, whereas at pH 3–7 the equilibrium is completely on the side of the contact ion pair and the first step in Scheme 2 can be considered unidirectional, i.e., $k_{\text{dis}} = 1/\tau_1$. Moreover, in 0.5 M H$_2$SO$_4$ no free ion pairs are formed due to the high proton concentration of the bulk solvent. At higher pH, the anion decays with $\tau_3 = 470$ ps, independent of the pH. In addition, all samples exhibit a longer-lived component with very small amplitude attributed to the geminate recombination56,57 or minor populations of photodegradation products. The fittings are very good in the anion emission range but much worse in the neutral range. This can be attributed to the limited time resolution of our instrument and inadequate fittings of the long-lived tails.

The model presented in Scheme 2 is qualitatively in good agreement with the data, but the limited time resolution of our TCSPC setup hinders the quantitative analysis of the rate constants. Faster techniques (fs-pump–probe or up-conversion) have been used to resolve these ultrafast components in related studies on photoacids.15,33,57,59,60 Another approach is to use mixtures of organic solvents and water to slow down the deprotonation kinetics.58

**Decays of the Ground-State Anion of EG-dHONI at Different pH Values.** The diffusion controlled back-protonation of the ground-state anion (Table 5) is well described in the literature.35,36 At low pH, the back-protonation exhibits pseudo-first-order kinetics also reported for HPTS at low pH. Fitting to an exponential function gives a lifetime of $\tau = 23$ ns at pH 3.0. The decay at intermediate pH is fitted as a mixture of first- and second-order reactions with an equation derived by Huppert et al.36 The pH of the sample was measured prior to deoxygenation, but the initial proton concentration was used also as a fitting parameter. The pH was 5.0 after sample preparation, but the proton concentration resulting from the fittings gave pH 5.4, indicating a slight increase in pH during deoxygenation. The second-order rate constant at pH 5.4 is $k_{\text{homin}} = 1.8 \times 10^{11}$ M$^{-1}$ s$^{-1}$. The decay at neutral pH exhibits pure diffusion limited bimolecular recombination with $k_{\text{homin}} = 1.9 \times 10^{10}$ M$^{-1}$ s$^{-1}$. The rate at neutral pH is comparable to that of HPTS ($k_{\text{homin}} = (1.84-2.06) \times 10^{11}$ M$^{-1}$ s$^{-1}$)58 at zero ionic strength.

**Possibility of the Formation of the Dianion of EG-dHONI.** No dianion was observed in any of the experiments. The compound undergoes hydrolysis of the imide group under strongly basic conditions before deprotonation of the second hydroxyl group is observed. Deprotonation of the first hydroxyl group increases the pK$_a$ of the second hydroxyl group deactivating the deprotonation both in the ground and excited states in the studied pH range. Similar observations have been reported for 4,5-dihydroxynaphthalene-2,7-disulfonic acid (chromotropic acid).61 For chromotropic acid, the pK$_a$ of the second hydroxyl group was found to be 15.6 without any photocid character.

**Quantum Chemical Calculations on Model Compounds.** Quantum chemical calculations (Table 6) reproduce the absorption spectra of EG-dHONI and EG-SHONI to high accuracy ($\Delta E < 0.06$ eV), supporting the choice of functional and basis set. Calculated emission energies are overestimated by ~0.2–0.4 eV. This could be due to the explicit solvent effects such as hydrogen bonding and solvation of the hydrogen bonded complex in the excited state.29 Although the bond lengths (C–O and O–H) are slightly altered in the excited state, the changes are negligibly small in the absence of a hydrogen bond or proton acceptor. An explicit solvent model combined with COSMO could possibly overcome these limitations but was out of the scope of the present study.

Frontier orbitals show the partial charge transfer character of the excited state resulting in photoacidity. The electron density of the hydroxyl oxygen is significantly decreased in the first excited state (HOMO → LUMO). The change in the Mulliken charge of the hydroxyl oxygen upon excitation possibly correlates with $\Delta pK_a$ (SHONI < dHONI), but more experimental data is required to establish stronger correlation. Nevertheless, the calculations suggest that attachment of a cyano group in the 6-position should strongly enhance the photoacidity. Similar experimental observations have been reported for cyano-functionalized 2-naphthols.12,21

**CONCLUSIONS**

We have studied both ground- and excited-state acid–base properties of three novel NI-derived “super” photoacids exhibiting negative pK$_a$’s. The pK$_a$ is not altered by N-substitution but is decreased upon sulfonation of the aromatic
The decay of the equilibrium state in DMSO also correlates with alcohols and DMSO. Good correlation is established between the parameters required to establish better correlations between the parameters with a larger set of compounds and with better time resolution are suitable for biological applications. More detailed studies on such as DMSO.

The deprotonation process both in DMSO and H₂O can be reasonably well explained with the two-step deprotonation model (Scheme 2). The first step corresponds to the initial relaxation to the equilibrium state between the neutral form and contact ion pair followed by a diffusion step resulting in the formation of the free ion pairs (at pH ≥ 3). The rate of decay of the equilibrium state in DMSO also correlates with pKₐ in this series of compounds. Slight disagreement in the data measured in the neutral vs anion wavelength ranges suggests a more complicated deprotonation mechanism (three-step model), but the initial processes are too fast (<25 ps) to be resolved in our experiments.

Our results support and complement the already available body of knowledge and understanding of photoacids reported in the literature. Nevertheless, these photoacids extend the ongoing field of research on “super” photoacids and offer robust and easily modifiable compounds with tunable acid-base (both ground and excited states), spectroscopic, and chemical properties. The substituent on the imide group of the super photoacids with tunable acid strength can be used to control the deprotonation rate in aprotic solvents such as DMSO.

REFERENCES


ASSOCIATED CONTENT

1 Supporting Information
Synthetic procedures and characterization of the compounds, experimental information, additional spectra of the photoacids, scheme of different species of EG-dHONI as a function of pH, and additional frontier orbitals. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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