Supporting Information for:

Excited-State Proton Transfer to Solvent from Phenol and Cyanophenols in Water

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Deconvolution analyses of PA waveform

The PA signal $S(t)$ of sample solutions is expressed as convolution integral between impulse response function $R(t)$ and time-dependent sample decay function $h(t)$.

$$S(t) = R(t) \otimes h(t) \tag{S1}$$

where $R(t)$ is given by the PA signal of photocalorimetric reference. In a sequential reaction model, $h(t)$ is given by

$$h(t) = \sum_{\mathrm{i}} \varphi_{\mathrm{i}} h_{\mathrm{i}}(t) = \frac{\varphi_1}{\tau_1}\exp\left(-\frac{t}{\tau_1}\right) + \frac{\varphi_2}{\tau_1 - \tau_2}\left[\exp\left(-\frac{t}{\tau_1}\right) - \exp\left(-\frac{t}{\tau_2}\right)\right] \tag{S2}$$

where $h_{\mathrm{i}}(t)$ is the sample decay function of the transient i with the lifetime of τ_{i} and φ_{i} is the fractional amplitude.

The ESPT cycle of hydroxyaromatic molecules can be analyzed according to a sequential reaction scheme:

$$\mathrm{ROH}^* + \mathrm{H_2O} \underset{\varphi_1}{\xrightarrow{\tau_1}} \mathrm{RO}^- + \mathrm{H_3O}^+ \underset{\varphi_2}{\xrightarrow{\tau_2}} \mathrm{ROH} + \mathrm{H_2O} \tag{S3}$$

where φ_1 is the PA signal amplitude for the proton transfer step with the time constant of τ_1, φ_2 is that for the proton recombination process with the time constant of τ_2. The parameters φ_1, τ_1, φ_2, τ_2 can be calculated from the sample and reference PA waveforms by means of the deconvolution method. The deconvolution analyses of the waveform were performed using the Sound Analysis 3000 software (Quantum Northwest). Figure S1(a) shows the PA signal of photocalorimetric reference $Na_2Cr_2O_7$ in H_2O (pH 4.0) at 10°C, which corresponds to the impulse response function $R(t)$, and the PA signal $S(t)$ of *o*-CNOH in H_2O (pH 4.0) at 3.9°C ($T_{\beta=0}$). Figure S1(b) shows the deconvoluted sample signals:

$$S(t) = S_1(t) + S_2(t) \tag{S4}$$

where $S_1(t)$ is the negative volume change signal (φ_1 = -0.476 and τ_1 < 1ns) due to the photo-induced proton transfer reaction, and $S_2(t)$ is the positive volume change signal (φ_2 = 0.471 and τ_2 = 217ns) arising from the proton recombination reaction.

By applying the deconvolution analysis to eq 9 in the text, the following equation is derived:

$$\varphi_1 E_\lambda = \Delta V_\mathrm{r}\left(\frac{C_p\rho}{\beta}\right) \tag{S5}$$

In the two-temperature method using deconvolution analyses, the structural volume change per absorbed Einstein (ΔV_r) can be determined from the plot of $\varphi_1 E_\lambda$ versus the thermodynamic parameters term ($C_\mathrm{p}\rho / \beta$). In Figure S2 the values of $\varphi_1 E_\lambda$ obtained for the proton dissociation step of *o*-CNOH and 1-naphthol (1-NpOH) in H_2O (pH 4.0) are plotted following eq S5. From the slopes of the straight lines, ΔV_r were obtained as -5.0 and -11.1 mL Einstein^{-1} for *o*-CNOH and 1-naphthol, respectively. By using the reaction quantum yield (Φ_R = 0.68) for 1-NpOH, which was estimated by transient absorption measurements, the structural volume change per photoconverted mole ΔV_R of 1-NpOH was obtained to be -16.4 mL mol^{-1}.

Figure Captions

Fig. S1: (a) PA signal amplitudes of photocalorimetric reference $Na_2Cr_2O_7$ in H_2O (pH 4.0) at 10°C (solid line) and *o*-CNOH in H_2O (pH 4.0) at 3.9°C (broken line), and (b) the deconvoluted sample signals $S_1(t)$ and $S_2(t)$. PA signal amplitude of *o*-CNOH in H_2O is shown both in (a) and (b) as broken line.

Fig. S2: $\varphi_1 E_\lambda$ value vs ($C_p\rho/\beta$) for the PA signals obtained by excitation of *o*-CNOH (open circle) and 1-NpOH (open triangle) in H_2O (pH 4.0).

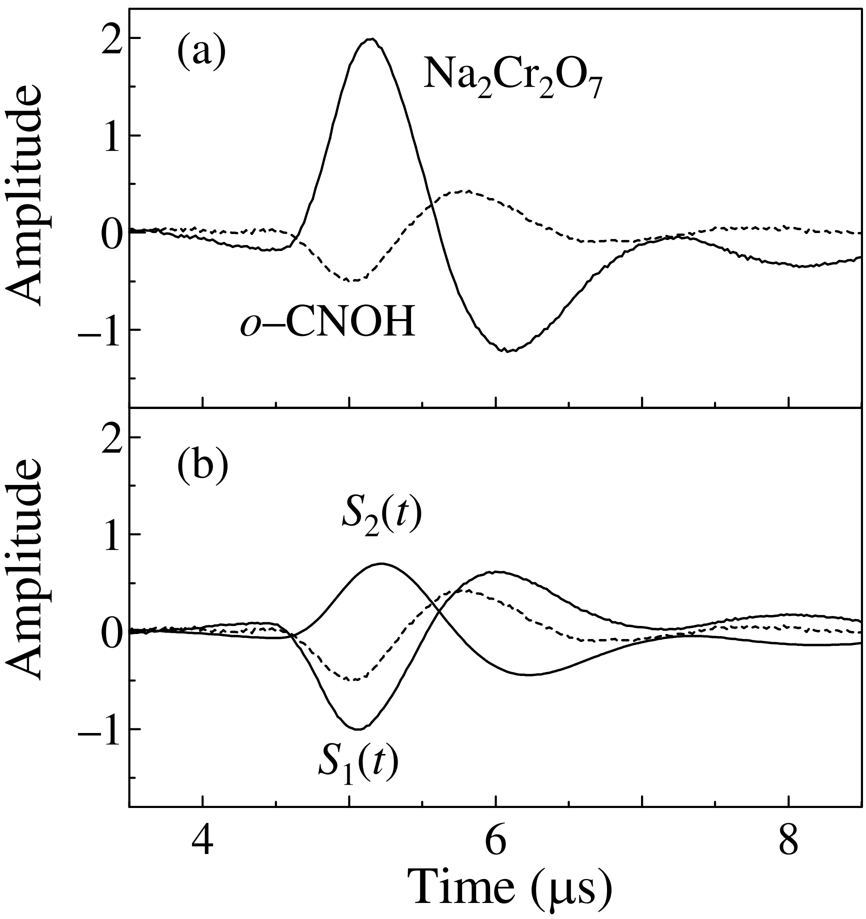
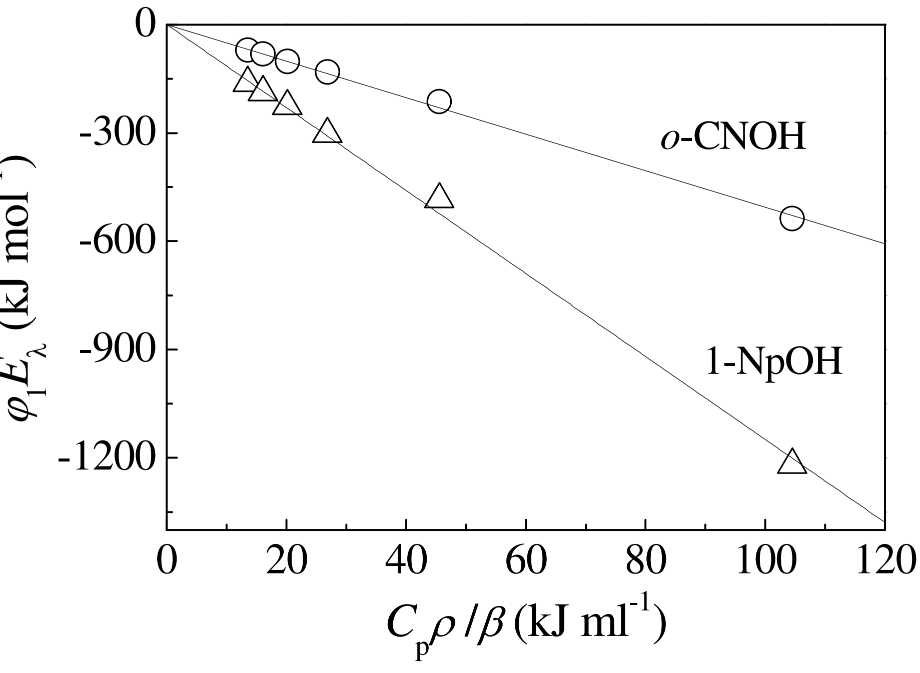


Figure S1   S. Kaneko *et al.*



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