Electronic Supplementary Information

Spectroscopic study of the excited state proton transfer processes of (8-bromo-7-hydroxyquinolin-2-yl)methyl-protected phenol in aqueous solutions

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Figure S1. UV-Vis absorption spectrum of BHQ-OPh in acetonitrile.

Figure S2. UV-Vis absorption spectra of BHQ-OPh in acetonitrile and 1:1 acetonitrile/PBS (pH 7.4).

Figure S3. Titration of BHQ-OPh (left) and BHQ-OAc (right) to determine the pK\textsubscript{a} of the phenolic proton. BHQ-OPh or BHQ-OAc was dissolved in buffers of known pH, and its spectral maxima were noted by UV-vis at 331 (phenol) and 371 nm (phenolate) (or 330 and 368 nm for BHQ-OAc). The ratio of the absorbance at the two reference wavelengths was plotted vs pH of the buffer. The plot is fitted with a sigmoidal regression and the pK\textsubscript{a} was calculated by solving for the inflection point. Buffers (pH): phosphate (3.91, 6.73, 7.32, and 7.86), acetate (5.13 and 5.65), citrate (6.17), borate (8.59 and 9.47).
Figure S4. Simulated absorption spectrum of BHQ-Oph (N) obtained from TD-DFT calculation at the level of B3LYP/6-311G**.

Figure S5. Simulated absorption spectrum of BHQ-Oph (A) obtained from TD-DFT calculation at the level of B3LYP/6-311G**
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<tr>
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<th>84 (LUMO)</th>
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<th>83 (HOMO)</th>
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<th>82 (HOMO-1)</th>
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**Figure S6.** Frontier molecular orbitals of the strongest oscillator strength transition at 227.78 nm for BHQ-OPh (N).

**Figure S7.** Comparison between low power 266-nm resonance Raman spectrum of BHQ-OPh in 1:1 acetonitrile/water and the DFT calculated Raman spectra of N(S\textsubscript{0}) and A(S\textsubscript{0}) of BHQ-OPh.
**Figure S8.** Comparison between low power 240-nm resonance Raman spectrum of BHQ-OPh in 1:1 acetonitrile/water (pH 5) solution and the DFT calculated Raman spectrum of N(S$_{0}$) of BHQ-OPh.

**Figure S9.** Simulated absorption spectrum for the T$_{1}$ state of BHQ-OPh (N) obtained from TD-DFT calculation at the level of B3LYP/6-311G**

**Figure S10.** Simulated absorption spectrum for the T$_{1}$ state of BHQ-OPh (A) obtained from TD-DFT calculation at the level of B3LYP/6-311G**
Figure S11. ns-TA spectra of BHQ-OPh in PBS (pH 7.4) after 266-nm excitation.

Figure S12. Fit of the ns-TA spectra in Fig. 4c to determine the rate constant for the decay of the T₁ state of BHQ-OPh (T).

Curve fit:
\[ y = y_0 + A_1 e^{-(x-x_0)/t_1} \]

\[ y_0 = 0.007030 \]
\[ x_0 = 51.73233 \]
\[ A_1 = 0.056530 \]
\[ t_1 = 874.97694 \]

Figure S13. Comparison between high power 240-nm resonance Raman spectrum of BHQ-OPh in acetonitrile and the DFT calculated Raman spectra of the T₁ and S₀ states of BHQ-OPh (N).
Figure S14. ns-EM spectra of BHQ-OPh in PBS (pH 7.4) after 266-nm excitation.
Figure S15. fs-TA spectra of BHQ-OPh in 1:1 acetonitrile/PBS (pH 7.4) after 266-nm excitation. (a) The growth of the 355-nm absorption band within 1 ps results from excitation from the ground state BHQ-OPh (A). (b) Subsequently, there is a conversion with an emission band at 450 nm and an absorption band at 635 nm. Based on the assignments for the ns-EM spectra in 1:1 acetonitrile/PBS (pH 7.4) (Fig. 7), the emission band at 450 nm is attributed to the fluorescence from the S\textsubscript{1} state of BHQ-OPh (A). Hence, the conversion in (b) can be assigned to the formation of the S\textsubscript{1} state of BHQ-OPh (A). (c) The growing features at 410 and 528 nm are assigned to the T\textsubscript{1} state of BHQ-OPh (A) based on the ns-TA spectra (Fig. 4). The conversion in (c) indicates the intersystem crossing from the S\textsubscript{1} state of BHQ-OPh (A) to the T\textsubscript{1} state of BHQ-OPh (A).
Figure S16. Comparison between the high power 240-nm resonance Raman spectrum of BHQ-OPh in 1:1 acetonitrile/PBS (pH 7.4) and the DFT calculated Raman spectra of the T₁ and S₀ states of BHQ-OPh (A).

Figure S17. fs-TA spectra of BHQ-OPh in 1:1 acetonitrile/water (pH 5.0) after 266-nm excitation.
**Scheme S1.** Proposed mechanism of BHQ-OPh photoprocesses in acetonitrile.

**Table S1.** Selected electronic transition energies, oscillator strength in the region of 210-310 nm, and molecular orbital transitions for the strongest oscillator strength transition at 227.78 nm obtained from (U)B3LYP/6-311G** TD-DFT calculations for the neutral form of BHQ-OPh.

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<th>Excitation Energy (nm)</th>
<th>Oscillator Strength</th>
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<tr>
<td>211.42</td>
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