Novel Chemosensor for Hypochlorite Anion Based on a Fluorescent Rhodamine 6G Reporter in Water

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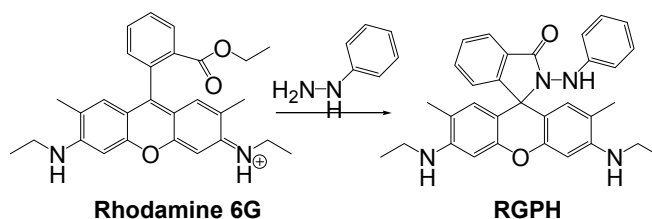
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Materials and methods

1. Instruments

All solvents and reagents (analytical grade and spectroscopic grade) were obtained commercially and used as received unless otherwise mentioned. NMR spectra were recorded on a Bruker spectrometer at 400 (^{1}H NMR) MHz and 100 (^{13}C NMR) MHz. Chemical shifts (δ values) were reported in ppm down field from internal Me_4Si (^{1}H and ^{13}C NMR). HRMS spectra were recorded on a Varian QFT-ESI mass spectrometer and a QTOF mass spectrometer. Elemental analyses were performed on a Vanio-EL elemental analyzer (Analysensysteme GmbH, Germany). UV absorption spectra were recorded on a UV-2550 UV-VIS spectrophotometer (Shimadzu, Japan). Fluorescence measurements were performed using an F-4600 fluorescence spectrophotometer (Hitachi, Japan) equipped with a quartz cell (1 cm × 1 cm). Melting points were recorded on a Boetius Block apparatus and are uncorrected.

2. Synthesis of RGPH

Rhodamine 6G   RGPH

To a 100 mL reactor, was charged rhodamine 6G (0.60 g, 1.2 mmol), phenyl hydrazine (5 mL, 50 mmol) and ethanol (20 mL). The reaction mixture was heated to reflux for 7 h. The solvent was removed under reduced pressure. The residue was disolved in dichloromethane (50 mL), and washed with saturated $NaHCO_3$ solution. The organic phase was separated. The water phase was extracted with dichloromethane (30 mL). The

combined organic phase was washed with water (50 mL × 2) and dried over anhydrous MgSO$_4$. After filtration, the filtrate was condensed to dryness. The residue was triturated with acetonitrile. The precipitate was collected by filtration, and the solid was washed with acetonitrile (5 mL × 2), dried under vacuum. **RGPH** was obtained as yellow powder in 88% yield; mp. 179-180 °C; HRMS: m/z [M + H]$^+$ =505.2596; Calcd: 505.2598; ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 1.29 (t, 6H, J = 7.2 Hz, NCH$_2$CH$_3$), 1.92 (s, 6H, CH$_3$), 3.17 (m, 4H, J = 7.2 Hz, NCH$_2$CH$_3$), 5.30 (s, 2H, NHCH$_2$), 5.31(s, 1H, NHC$_6$H$_5$), 6.29 (s, 4H, xanthene-H), 6.49 (d, 2H, J = 8.0 Hz, Ar-H), 6.65 (t, 1H, J = 7.2 Hz, Ar-H), 6.91(t, 2H, Ar-H), 7.17 (d, 1H, J = 4.0 Hz, Ar-H), 7.54-7.62 (m, 2H, Ar-H), 8.02 (d, 1H, J = 4.0 Hz, Ar-H). ^{13}C NMR (100 MHz, CDCl$_3$, ppM): δ 167.2, 152.6, 150.8, 147.2, 147.1, 147.1, 147.8, 133.3, 130.5, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 124.5, 123.4, 120.5, 118.1, 114.7, 106.1, 97.3, 66.6, 53.5, 38.7, 16.8, 14.7. Anal. Calcd for C$_{32}$H$_{32}$N$_4$O$_2$: C, 76.16%; H, 6.39%; N, 11.10%. Found: C, 76.09%; H, 6.36%; N, 10.86%.
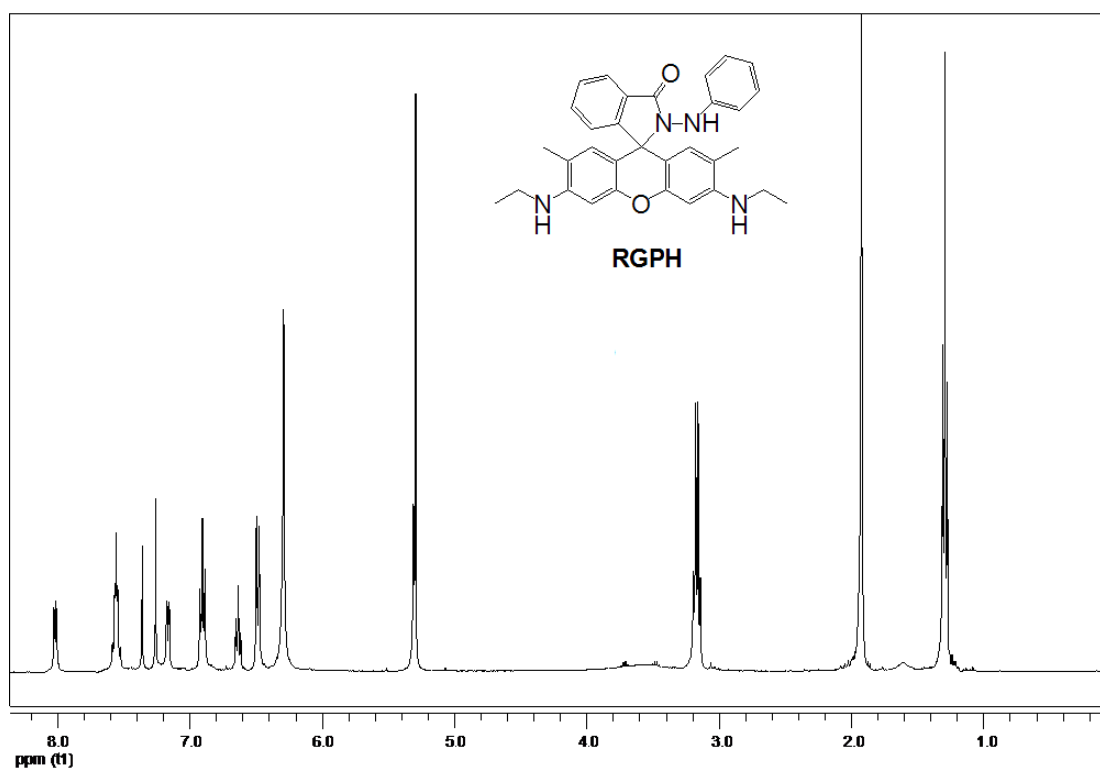

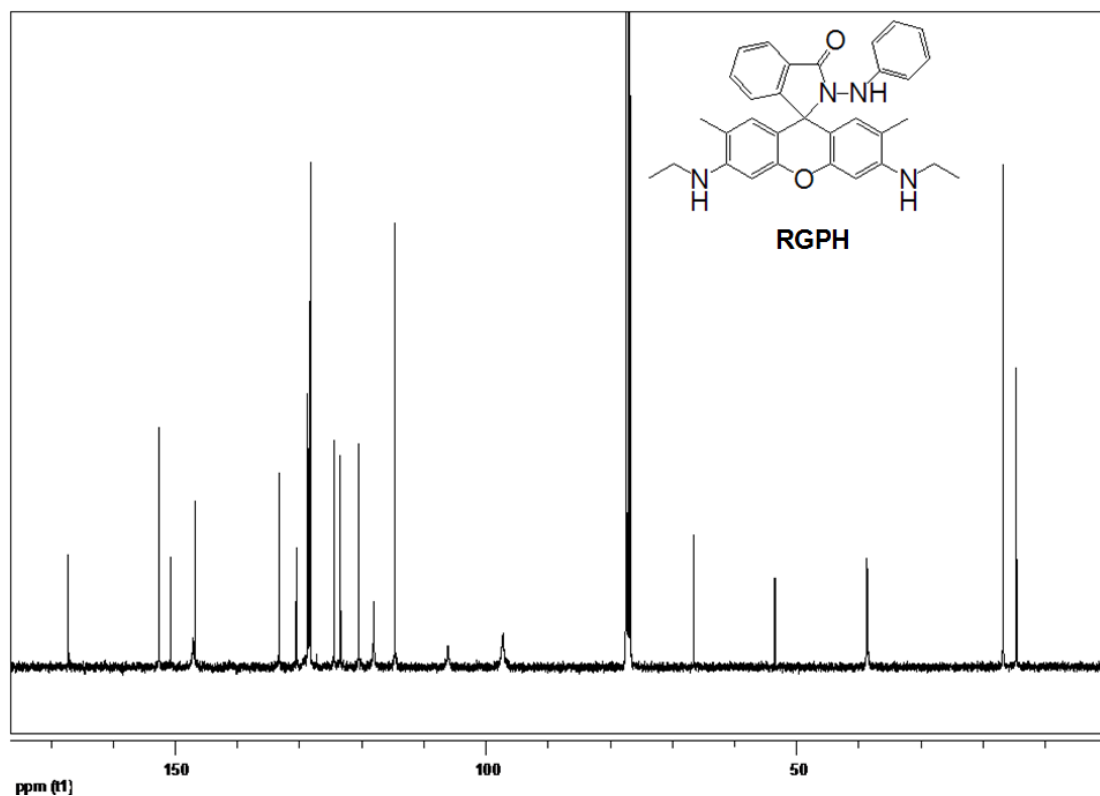**Figure S1**. ^{1}H NMR of **RGPH** (400 MHz, CDCl$_3$).

Figure S2. ^{13}C NMR of **RGPH** (100 MHz, CDCl$_3$).
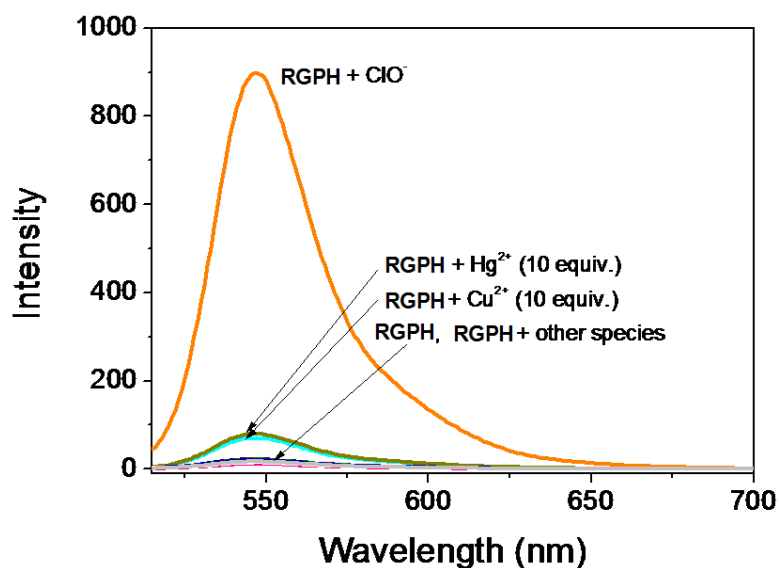

Figure S3. Emission spectra of **RGPH** (5 μM) with addition of sodium salts of Cl$^-$, ClO$_4^-$, H$_2$O$_2$, NO$_2^-$, NO$_3^-$ and SO$_4^{2-}$ (100 equiv.), ClO$^-$ (3.0 equiv.), nitrate salts of Ca^{2+}, K$^+$, Mg^{2+}, Pb^{2+}, Ni^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}, Hg^{2+} and TBHP and H$_2$O$_2$ (10 equiv.) in H$_2$O with an excitation at 505 nm.
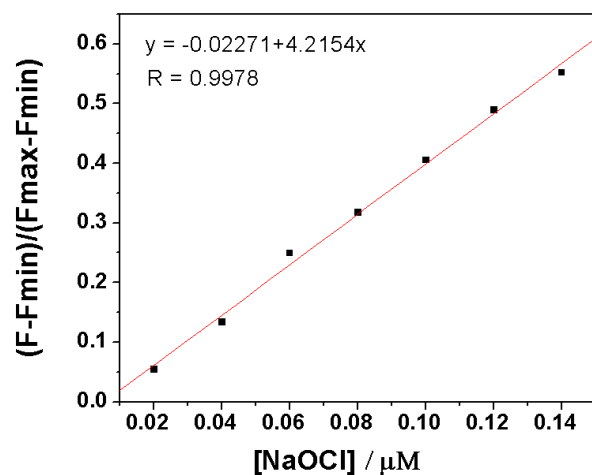
Figure S4. Emission (at 547 nm) of **RGPH** at different concentrations of ClO⁻ (0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14 μM) added, normalized between the minimum emission (0.0 μM ClO⁻) and the emission at 0.14 μM ClO⁻. The detection limit was estimated to be 5.0×10^{-9} M.
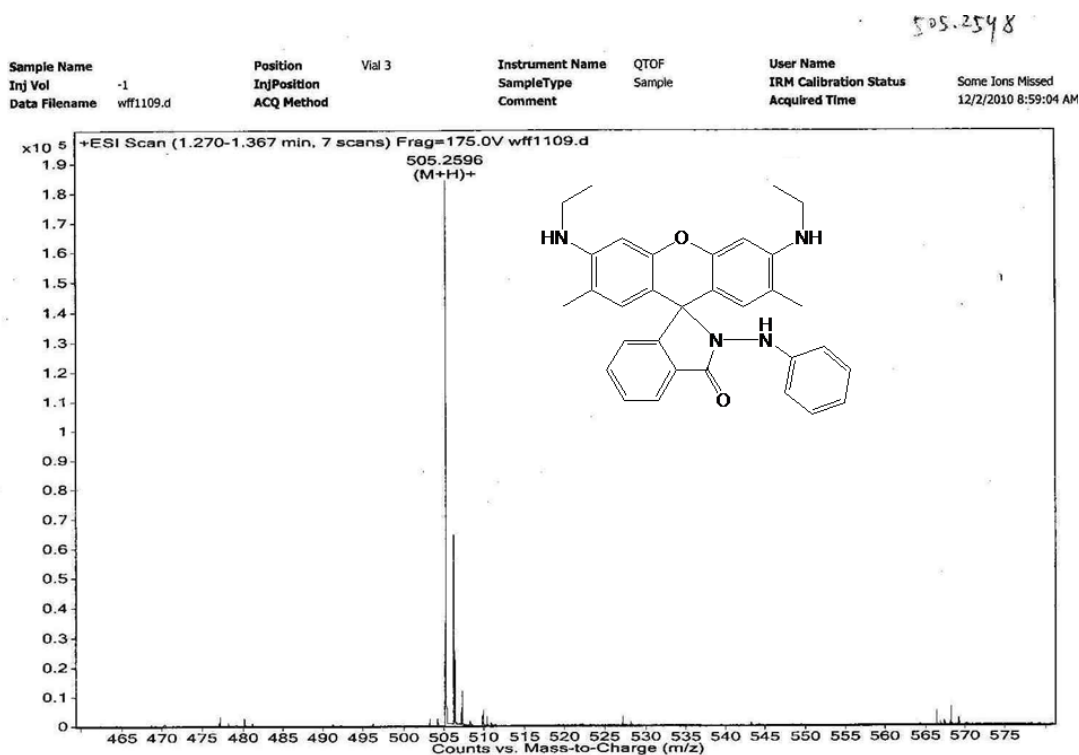

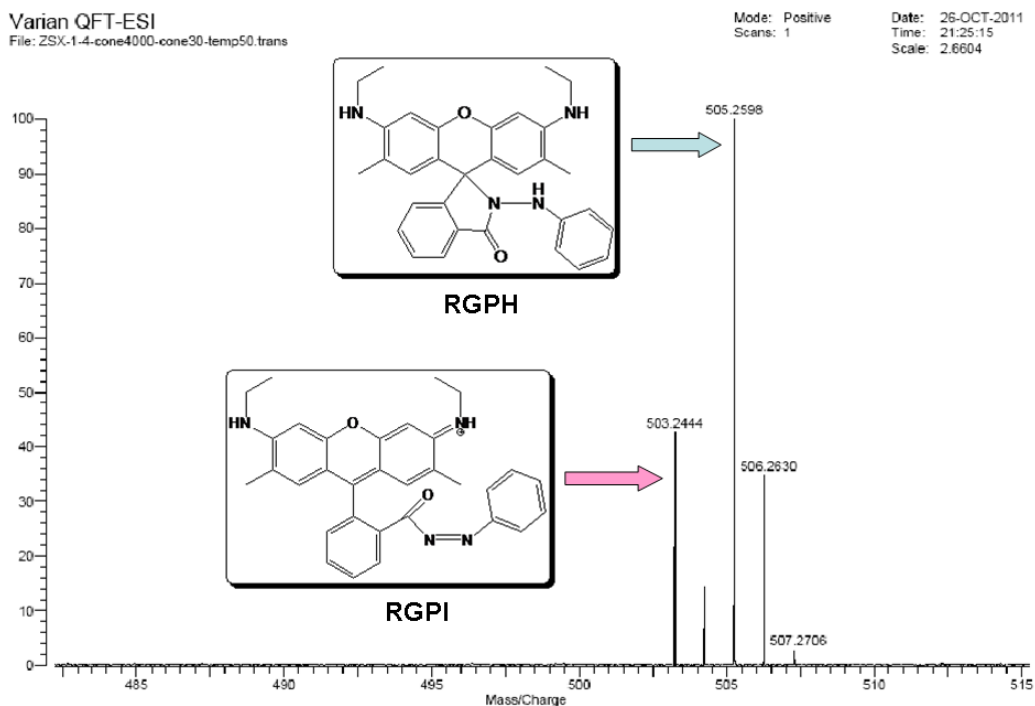**Figure S5**. HRMS spectra of **RGPH**. The peak (m/z) at 505.2596 corresponds to $[M + H]^+$ ion (Calcd: 505.2598).

Figure S6. HRMS spectra of the reaction mixture of **RGPH** with ClO⁻. The peak (m/z) at 503.2444 corresponds to the oxidized form of [**RGPI** + H]⁺ ion (Calcd: 503.2444). The peak (m/z) at 505.2598 corresponds to [**RGPH** + H]⁺ ion (Calcd: 505.2598).

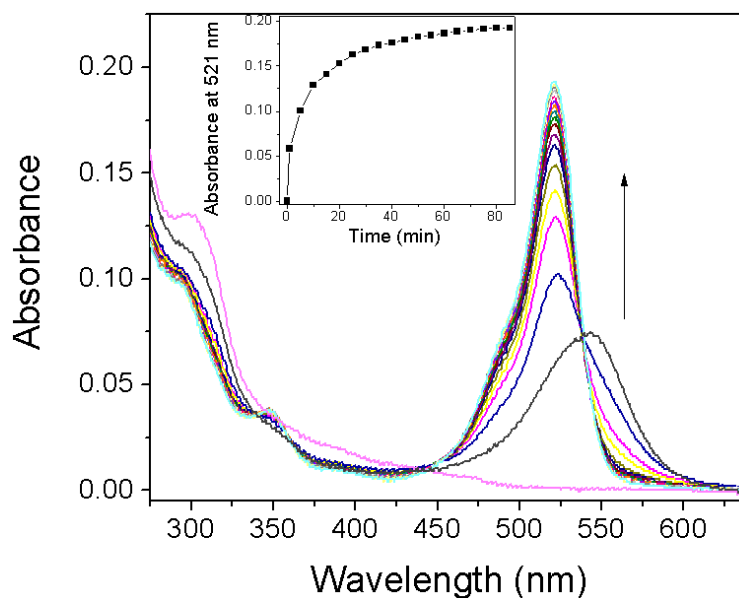**Figure S7**. Time-dependent absorption spectra of **RGPH** (10 μM) in the presence of ClO⁻ (3.0 equiv) in H₂O at 25 °C. Inset: absorbance at 521 nm at 0, 1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85 min.

A   B
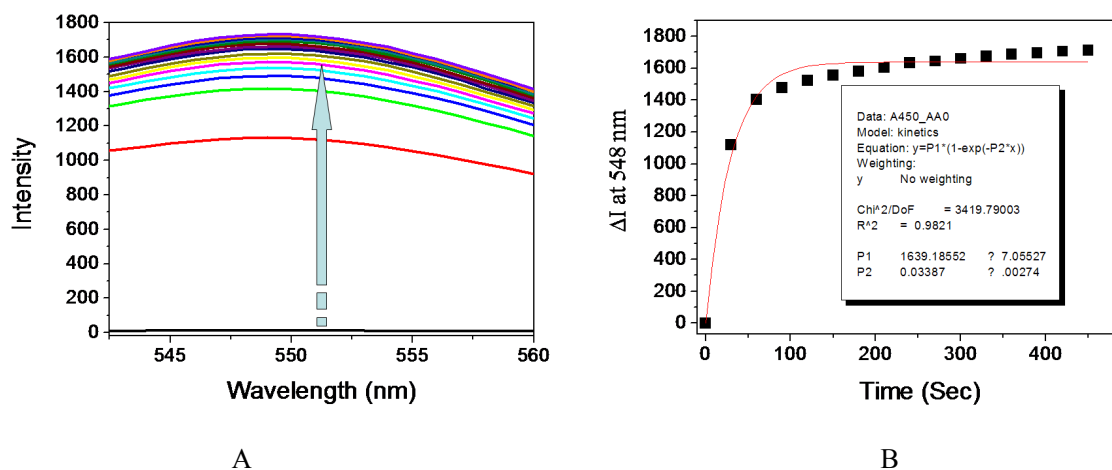
Figure S8. The reaction kinetic measurements of **RGPH** with ClO$^-$ under pseudo-first-order conditions by fluorescence spectra. A) Time-dependent changes in the fluorescence spectra and B) fluorescent intensity at λ = 548 nm observed from the reaction between **RGPH** (5.0 μM) and ClO$^-$ (600 μM) in H$_2$O at T = 298 K. The gray curve overlaid on the experimental data points is theoretical fit generated using k_{obs} =3.387 $\times$ 10^{-2} s^{-1}.
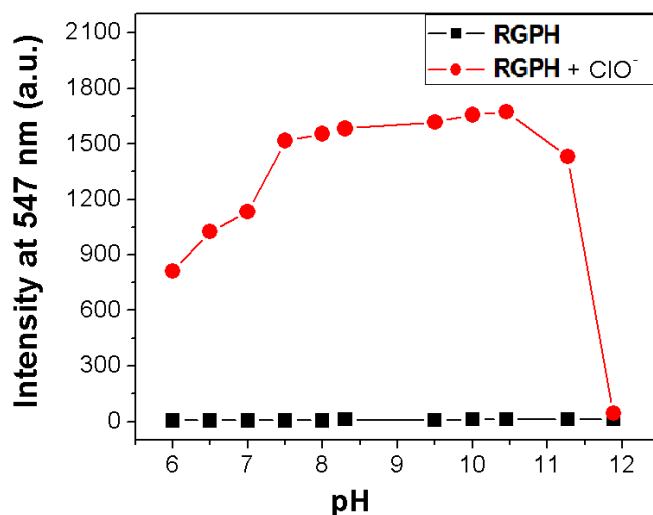

Figure S9. Profile of pH dependence of the fluorescence intensity of **RGPH** (5 μM) at 547 nm in the absence and presence of ClO$^-$ (3.0 equiv.) in H$_2$O.
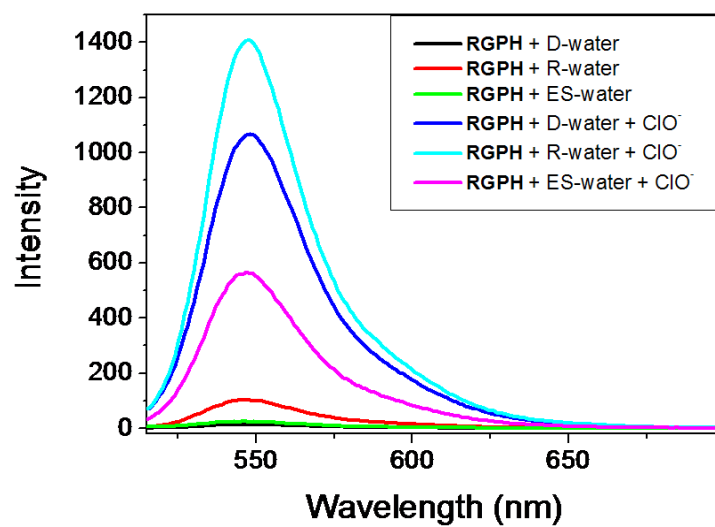
Figure S10. Response of **RGPH** (5 μM) in the absence and in the presence of ClO$^-$ (3 equiv.) in natural water samples.