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

Fangfang Wei,a Yan Lu,*a Song He, a Liancheng Zhaoa,b and Xianshun Zeng*a

a School of Materials Science & Engineering, Tianjin University of Technology, Tianjin 300384, China.
b School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China.

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 (1H NMR) MHz and 100 (13C NMR) MHz. Chemical shifts (δ values) were reported in ppm down field from internal Me₄Si (1H and 13C 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

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 dissolved in dichloromethane (50 mL), and washed with saturated NaHCO₃ 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 MgSO4. 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; 1H NMR (400 MHz, CDCl3, ppm): δ 1.29 (t, 6H, J = 7.2 Hz, NCH2CH3), 1.92 (s, 6H, CH3), 3.17 (m, 4H, J = 7.2 Hz, NCH2CH3), 5.30 (s, 2H, NHCH2), 5.31(s, 1H, NHCH2H5), 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). 13C NMR (100 MHz, CDCl3, ppm): δ 167.2, 152.6, 150.8, 147.2, 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 C32H32N4O2: C, 76.16%; H, 6.39%; N, 11.10%. Found: C, 76.09%; H, 6.36%; N, 10.86%.

![Figure S1. 1H NMR of RGPH (400 MHz, CDCl3).](image-url)
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 \(\mu\)M) added, normalized between the minimum emission (0.0 \(\mu\)M ClO\(^{-}\)) and the emission at 0.14 \(\mu\)M ClO\(^{-}\). The detection limit was estimated to be 5.0 \(\times\) 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.
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 $\lambda = 548$ nm observed from the reaction between RGPH (5.0 $\mu$M) and ClO⁻ (600 $\mu$M ) in H₂O 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 $\mu$M) at 547 nm in the absence and presence of ClO⁻ (3.0 equiv.) in H₂O.
Figure S10. Response of RGPH (5 µM) in the absence and in the presence of ClO⁻ (3 equiv.) in natural water samples.