Supporting Information for

An arylboronate locked fluorescent probe for hypochlorite

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Table of Contents

Experimental Section

Table S1. Some fluorescent probes for ClO⁻ detection.

Figure S1. ¹H NMR of R1 in DMSO-d6.

Figure S2. ¹H NMR of R1 in CD3OD.

Figure S3. HRMS of probe R1. Calculated for C25H28BN2O3 ([M+H]⁺): 415.2193, observed 415.2209.

Figure S4. Reaction between R1 and H2O2. a) TLC analysis of the reaction between R1 and H2O2; b) Low-field region of the ¹H NMR spectra of R1 and isolated product of R1+H2O2 (R1-OH) in DMSO-d6.

Figure S5. ¹H NMR of the purified reaction product of R1+H2O2 in DMSO-d6, which was determined to be R1-OH.

Figure S6. MS of the purified reaction product of R1+H2O2, which was determined to be R1-OH. Calculated for C19H13N2O2 ([M-H]⁻): 303.3, observed 303.0.

Figure S7. Fluorescence titration profile of R1 (1 μM) with an increasing amount of H2O2 (0 equiv. – excess amount) in EtOH/H2O (4:1, v:v).

Figure S8. Calibration curve of R1 (1 μM) with increasing amount of ClO⁻ in EtOH/H2O (4:1, v:v). Inset: linear response range.

Figure S9. Calibration curve of R1 (0.5 μM) with increasing amount of ClO⁻ in EtOH/H2O (4:1, v:v). Inset: linear response range.

Figure S10. UV-visible spectral titration profile of R1 (1 μM) with an increasing amount of ClO⁻ (0-60 equiv.) in EtOH/H2O (4:1, v:v). a) 0-24 equiv. of ClO⁻; b) 24-60 equiv. of ClO⁻.

Figure S11. Fluorescence spectra (normalized) of R1+ClO⁻ and R1-OH+ClO⁻ in EtOH/H2O (4:1, v:v).

Figure S12. Low-field region of the ¹H NMR spectra of R1 (20 mM) in DMSO-d6 upon successive addition of NaClO solution.

Figure S13. Low-field region of the ¹H NMR spectra of the isolated main reaction product of R1+ClO⁻ (60 equiv.) in DMSO-d6.

Figure S14. MS of the reaction products of R1+ClO⁻. The percentages of R1-OHCl3 increased with the addition of more equiv. of ClO⁻.

Figure S15. Selectivity of R1-OH toward ClO⁻ in EtOH/H2O (4:1, v:v). a) Emission spectral changes of R1-OH (1
μM) after addition of 60 equiv. of various ROS species; b) Corresponding fluorescence intensity ratio of F_{532}/F_{454}.

**Figure S16.** Fluorescence emission intensity of R1-OH (1 μM) at 454 nm over a pH range of 2.5–12.5.

**Figure S17.** Fluorescence emission intensity of R1 (1 μM, black squares, at 481 nm) and R1+ClO⁻ (60 equiv., red dots, at 532 nm) over a pH range of 2.5–12.5.

**Figure S18.** Fluorescence intensity ratio of F_{532}/F_{481} of R1 (1 μM) after addition of 60 equiv. of ClO⁻ in EtOH/H₂O (4:1, v:v) as a function of time.

**Figure S19.** Plot shows the fluorescence intensity of R1 at 481 nm under continuous 365 nm UV light irradiation during 4 h.

**References**
Experimental Section

General. Commercially available solvents and reagents were used without further purification. Deuterated solvents for NMR measurements were purchased from J & K Scientific (Shanghai, China). UV-visible absorption spectra were recorded on a UV-visible spectrophotometer (Beijing Purkinje General Instrument Co. Ltd., China). Fluorescence measurements were performed on a HITACHI F-4600 fluorescence spectrophotometer with a quartz cuvette (path length = 1 cm). $^1$H NMR spectra were obtained using a Bruker AM300 spectrometer with tetramethylsilane (TMS) as an internal standard. High resolution mass spectrum (HRMS) was measured on a LTQ Orbitrap XL mass spectrometer. Mass spectra of the reaction products of $\text{R1}$ upon addition of $\text{ClO}^-$ were measured on an Agilent 6460 QQQ mass spectrometer. Compound $\text{R2}$ was synthesized according to the reported literature.

Synthesis of $\text{R1}$. In a dry 25 mL Schlenk tube, precursor $\text{R2}$ (73.4 mg, 0.2 mmol), bis(pinacolato)diboron (101 mg, 0.4 mmol), potassium acetate (60 mg, 0.6 mmol), and Pd(dppf)Cl$_2$ (3.6 mg, 0.005 mmol) were dissolved in 8 mL 1,4-dioxane. The reaction mixture was then heated to reflux for 2.5 h under N$_2$ protection. TLC analysis revealed that the raw material $\text{R2}$ was completely consumed. The solvent was then evaporated to dryness under vacuum. The crude product was purified by silica-gel (200-300 mesh) column chromatography using CH$_2$Cl$_2$ as the eluent to obtain pure probe $\text{R1}$ as yellow powder (72 mg, yield: 87%). UV-Vis (EtOH:H$_2$O, 4:1, v:v) $\lambda_{\text{max}}$ (nm): 388 nm.

$^1$H NMR (DMSO-d$_6$, 300 MHz) $\delta$: 8.63 (d, 1H, $J = 1.2$ Hz), 8.19 (dd, 1H, $J_1 = 8.5$ Hz, $J_2 = 1.74$ Hz), 8.02 (s, 1H), 7.86 (d, 1H, $J = 9.0$ Hz), 7.81 (dd, 1H, $J_1 = 7.5$ Hz, $J_2 = 0.84$ Hz), 7.75 (m, 2H), 7.2 (dd, 1H, $J_1 = 9.1$ Hz, $J_2 = 2.5$ Hz), 6.91 (d, 1H, $J = 2.4$ Hz), 3.12 (s, 6H), 1.39 (s, 12H).

HRMS: observed: 415.2209, calculated for C$_{25}$H$_{28}$BN$_2$O$_3$ ([M+H]$^+$) 415.2193.

Synthesis of $\text{R1-OH}$. $\text{R1}$ (20 mg, 0.05 mmol) was dissolved in 40 mL EtOH, and then 3 mL H$_2$O$_2$ (30%) was added. The mixed solution was stirred for 30 min at room temperature until the raw material $\text{R1}$ completely disappeared. A new product was detected by TLC analysis and purified by silica-gel (200-300 mesh) column chromatography using CH$_2$Cl$_2$/MeOH (20:1, v:v) as the eluent to obtain pure $\text{R1-OH}$ as yellow powder (13.2 mg, yield: 90%). $^1$H NMR (CD$_3$OD, 300 MHz) $\delta$: 9.79 (s, 1H), 8.48 (s, 1H), 8.00 (q, 1H), 7.92 (d, 1H, $J = 9.0$ Hz), 7.77 (d, 1H, $J = 9.0$ Hz), 7.53 (d, 1H, $J = 8.7$ Hz), 7.28 (q, 1H), 7.08 (d, 1H, $J= 2.1$ Hz), 6.97 (d, 1H, $J = 2.1$ Hz), 6.83 (q, 1H).

MS: observed: 303.0, calculated for C$_{19}$H$_{15}$N$_2$O$_2$ ([M-H]$^-$): 303.3.

Fluorescence Measurements. The fluorescence emission spectra of $\text{R1}$ and $\text{R1-OH}$ (1 $\mu$M) were measured at 25 °C in mixed solutions of EtOH/H$_2$O (4:1, v:v), with the excitation wavelength fixed at 370 nm. The slit width was 5 nm, and the PMT voltage was 500 V. Hypochlorite ($\text{ClO}^-$) and H$_2$O$_2$ were diluted from commercial available NaClO and H$_2$O$_2$ aqueous solutions, respectively. Other tested ROS species (‘$\text{O}_2^-$’, NO$^-$, ROO$^-$, ONOO$^-$, and HO$^-$) were freshly prepared according to the literature method.\textsuperscript{2,3}
Table S1. Some fluorescent probes for ClO⁻ detection.

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<th>Response type</th>
<th>Detection limit</th>
<th>Response time</th>
<th>pH range of probe only</th>
<th>pH range of probe + ClO⁻</th>
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<td>7-8</td>
<td>13</td>
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</table>
Figures

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**Figure S10.** UV-visible spectral titration profile of R1 (1 μM) with an increasing amount of ClO\textsuperscript{−} (0-60 equiv.) in EtOH/H\textsubscript{2}O (4:1, v:v). a) 0-24 equiv. of ClO\textsuperscript{−}; b) 24-60 equiv. of ClO\textsuperscript{−}.
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Figure S18. Fluorescence intensity ratio of F₅₃₂/F₄₈₁ of R1 (1 μM) after addition of 60 equiv. of ClO⁻ in EtOH/H₂O (4:1, v:v) as a function of time.
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