# Supporting Information for

# An arylboronate locked fluorescent probe for hypochlorite

Leilei Shi,[a#] Xin Li,[b#] Min Zhou,[a] Faheem Muhammad,[a] Yubin Ding,*[ac] and Hui Wei*[a]

[a] Department of Biomedical Engineering, College of Engineering and Applied Sciences, Collaborative Innovation Center of Chemistry for Life Sciences, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing, Jiangsu 210093, China. E-mail: weihui@nju.edu.cn; ybding@nju.edu.cn. Phone: +86-25-83593272. Fax: +86-25-83594648. Web: weilab.nju.edu.cn.

[b] Division of Theoretical Chemistry and Biology, School of Biotechnology, KTH Royal Institute of Technology, SE-10691 Stockholm, Sweden.

[c] Jiangsu Key Laboratory of Pesticide Science, College of Sciences, Nanjing Agricultural University, Nanjing, Jiangsu 210095, China.

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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/$H_2O$ (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 **R1** upon addition of $ClO^-$ were measured on an Agilent 6460 QQQ mass spectrometer. Compound **R2** was synthesized according to the reported literature.[1]

**Synthesis of R1.** In a dry 25 mL Schlenk tube, precursor **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 **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 $CH_2Cl_2$ as the eluent to obtain pure probe **R1** as yellow powder (72 mg, yield: 87%). UV-Vis (EtOH:$H_2O$, 4:1, v:v) $\lambda_{max}$ (nm): 388 nm. $^1$H NMR (DMSO-$d_6$, 300 MHz) δ: 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). $^1$H NMR ($CD_3OD$, 300 MHz) δ: 8.60 (s, 1H), 8.11 (dd, 1H, $J_1$ = 8.6 Hz, $J_2$ = 1.8 Hz), 7.99 (s, 1H), 7.87 (d, 1H, $J$ = 9.3 Hz), 7.78 (d, 2H, $J$ = 7.8 Hz), 7.70 (d, 1H, $J$ = 8.1 Hz), 7.30 (dd, 1H, $J_1$ = 9.2 Hz, $J_2$ = 2.7 Hz), 7.0 (d, 1H, $J$ = 2.4 Hz), 3.12 (s, 6H), 1.39 (s, 12H). HRMS: observed: 415.2209, calculated for $C_{25}H_{28}BN_2O_3$ ($[M+H]^+$) 415.2193.

**Synthesis of R1-OH. R1** (20 mg, 0.05 mmol) was dissolved in 40 mL EtOH, and then 3 mL $H_2O_2$ (30%) was added. The mixed solution was stirred for 30 min at room temperature until the raw material **R1** completely disappeared. A new product was detected by TLC analysis and purified by silica-gel (200-300 mesh) column chromatography using $CH_2Cl_2$/MeOH (20:1, v:v) as the eluent to obtain pure **R1-OH** as yellow powder (13.2 mg, yield: 90%)). $^1$H NMR (DMSO-$d_6$, 300 MHz) δ: 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 $C_{19}H_{15}N_2O_2$ ($[M-H]^-$): 303.3.

**Fluorescence Measurements.** The fluorescence emission spectra of **R1** and **R1-OH** (1 μM) were measured at 25 °C in mixed solutions of EtOH/$H_2O$ (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 ($ClO^-$) and $H_2O_2$ were diluted from commercial available NaClO and $H_2O_2$ aqueous solutions, respectively. Other tested ROS species ($^1O_2$, $O_2^{\bullet-}$, $NO^\bullet$, $ROO^\bullet$, $ONOO^-$, and $HO^\bullet$) were freshly prepared according to the literature method.[2, 3]

**Table S1.** Some fluorescent probes for $ClO^-$ detection.

| Response type | Detection limit | Response time | pH range of probe only | pH range of probe + $ClO^-$ | Reference |
|---|---|---|---|---|---|
| **Ratiometric** | 6.4 nM | ~2 min | 4.5-9 | 5-10 | Our probe |
| | 70 nM | ~100 s | 2-10.5 | 2-10.5 | 4 |
| | 0.12/0.84 nM | in seconds | 5-10 | 7-10 | 5 |
| | 40 nM | immediately | 2-10 | 4-8 | 6 |
| **Turn-off** | 0.7 μM | < 3 min | 6-9 | 6-7.46 | 7 |
| | 0.34 μM | rapidly | 3-10 | 6-8 | 8 |
| **Turn-on** | 18 nM | ~15 min | 3-12 | 6-8 | 9 |
| | 17.9 nM | ~1 min | 4-10 | 4-10 | 10 |
| | 0.2 μM | quickly | 5.5-9.3 | 5.5-9.3 | 11 |
| | 2.4 nM | ~30 min | 4-10 | 7-10 | 12 |
| | 0.3 μM | ~60 min | 3-9 | 7-8 | 13 |

## Figures

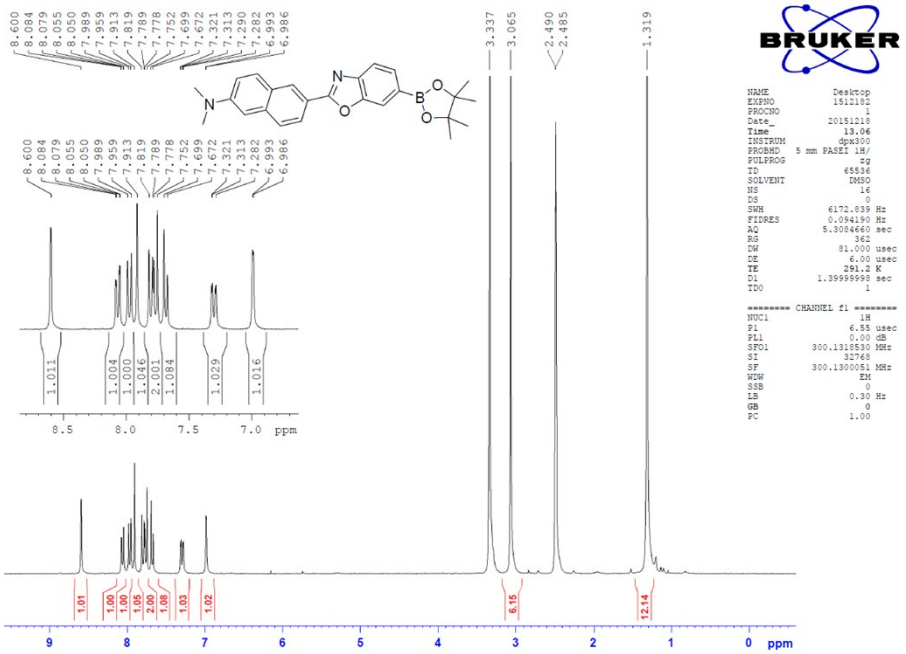

**Figure S1.** [1]H NMR of **R1** in DMSO-d6.

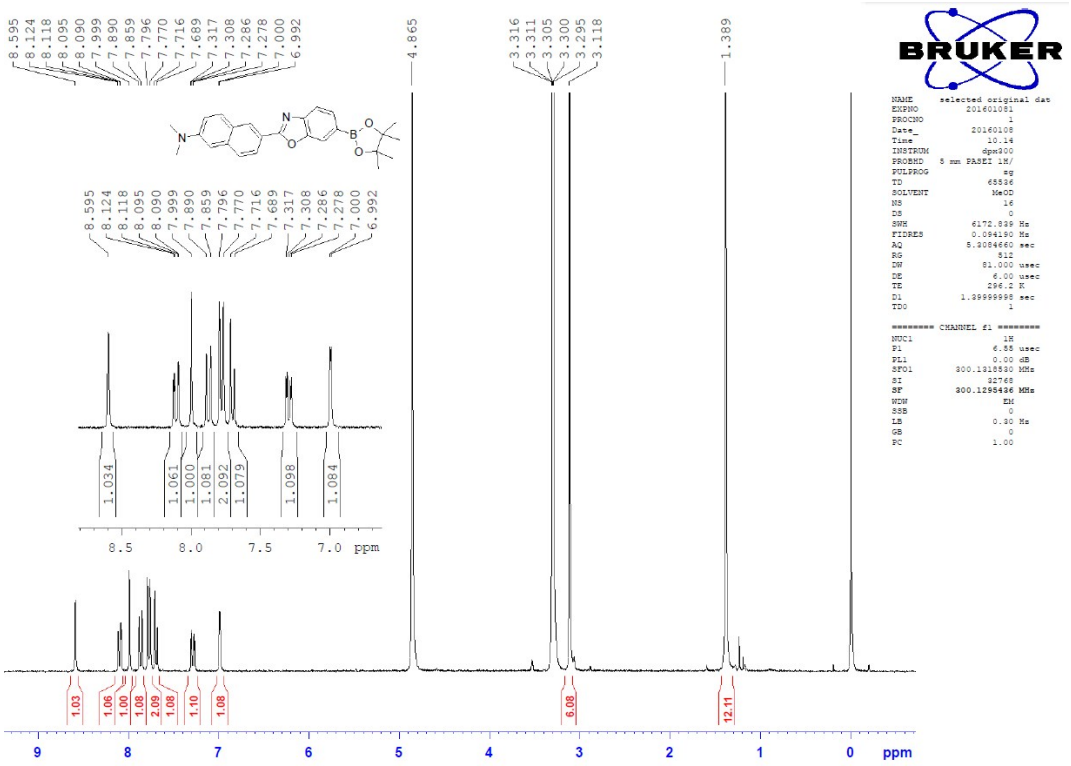

**Figure S2.** [1]H NMR of **R1** in $CD_3OD$.

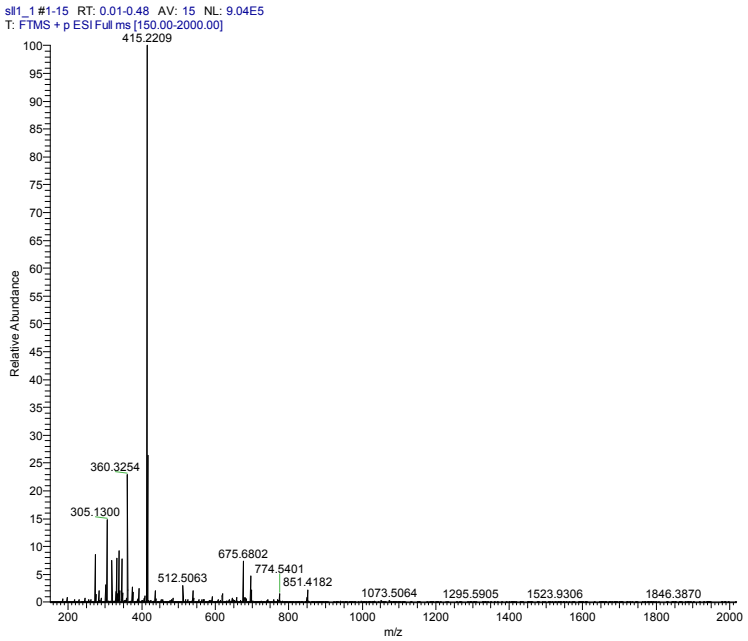


**Figure S3.** HRMS of probe **R1**. Calculated for $C_{25}H_{28}BN_2O_3$ ([M+H]$^+$): 415.2193, observed 415.2209.

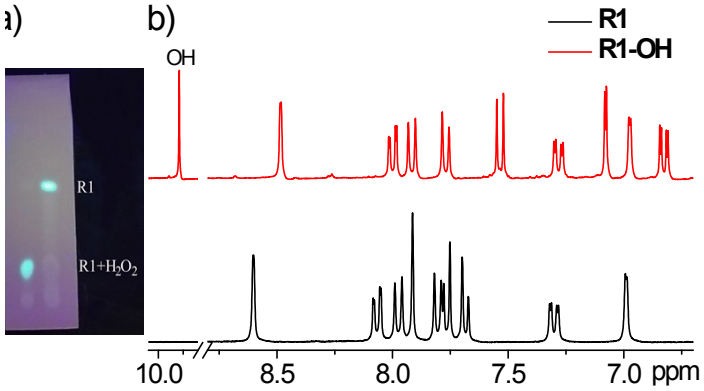


**Figure S4.** Reaction between **R1** and $H_2O_2$. a) TLC analysis of the reaction between **R1** and $H_2O_2$; b) Low-field region of the $^1$H NMR spectra of **R1** and isolated product of **R1**+$H_2O_2$ (**R1-OH**) in DMSO-d6.

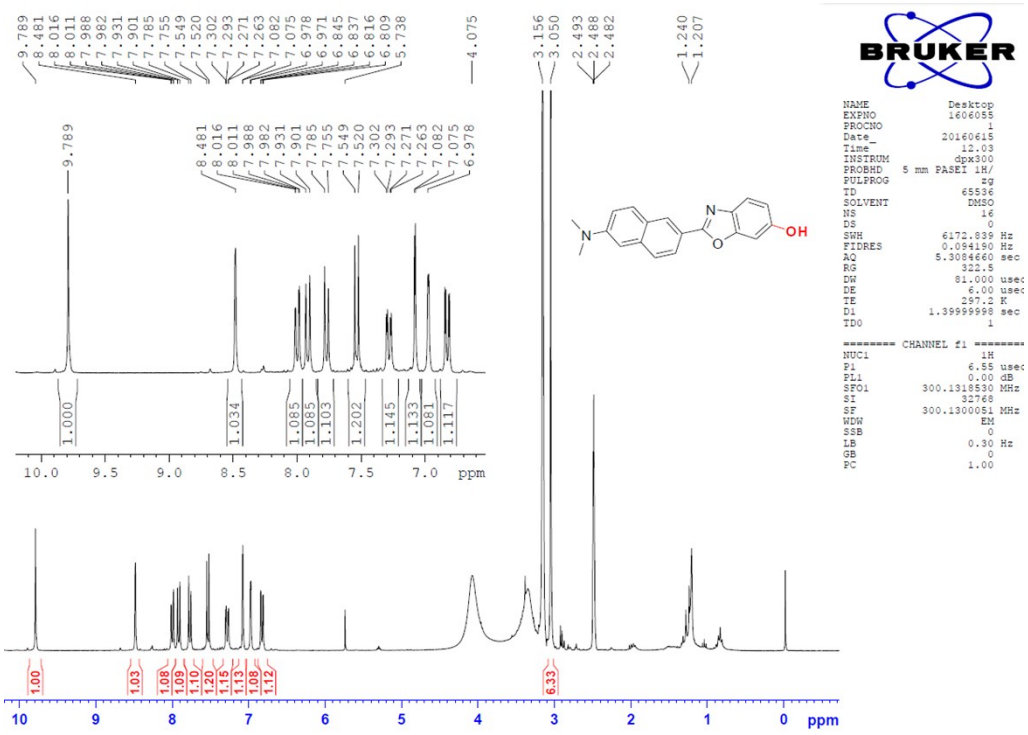


**Figure S5.** $^{1}$H NMR of the purified reaction product of **R1**+$H_2O_2$ in DMSO-d6, which was determined to be **R1-OH**.

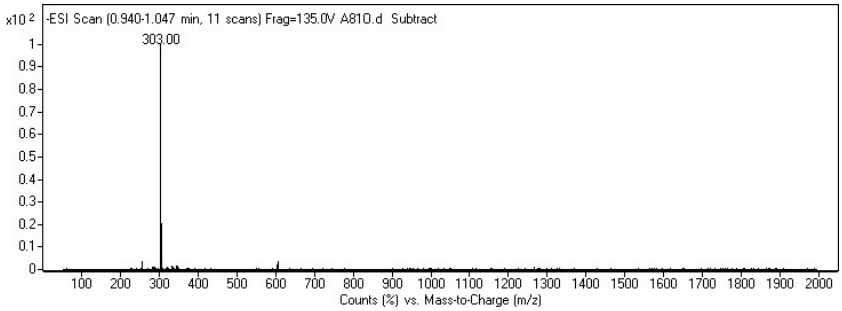


**Figure S6.** MS of the purified reaction product of **R1**+$H_2O_2$, which was determined to be **R1-OH**. Calculated for $C_{19}H_{15}N_2O_2$ ([M-H]$^-$): 303.3, observed 303.0.

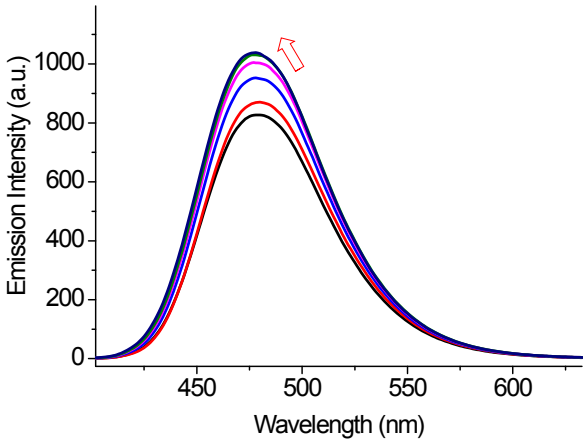


**Figure S7.** Fluorescence titration profile of **R1** (1 μM) with an increasing amount of $H_2O_2$ (0 equiv. – excess amount) in EtOH/$H_2O$ (4:1, v:v).

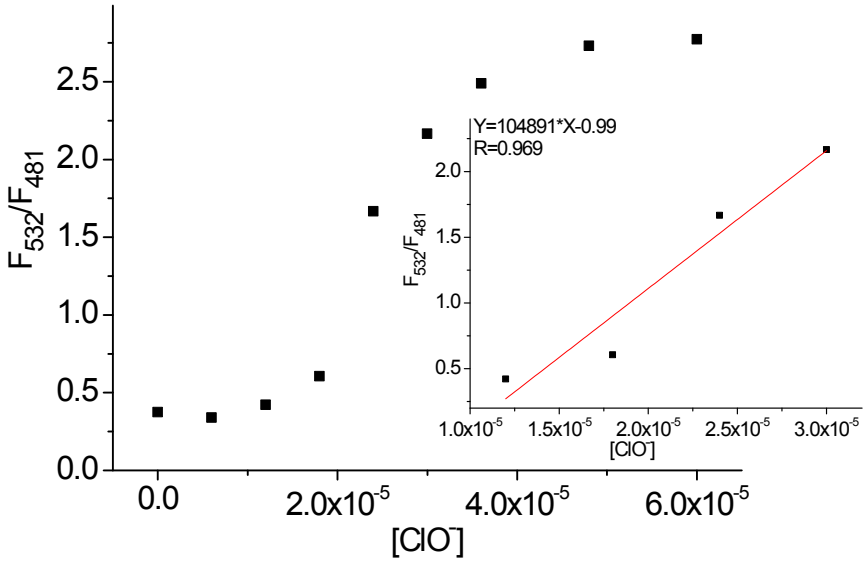


**Figure S8.** Calibration curve of **R1** (1 μM) with increasing amount of $ClO^-$ in EtOH/$H_2O$ (4:1, v:v). Inset: linear response range.

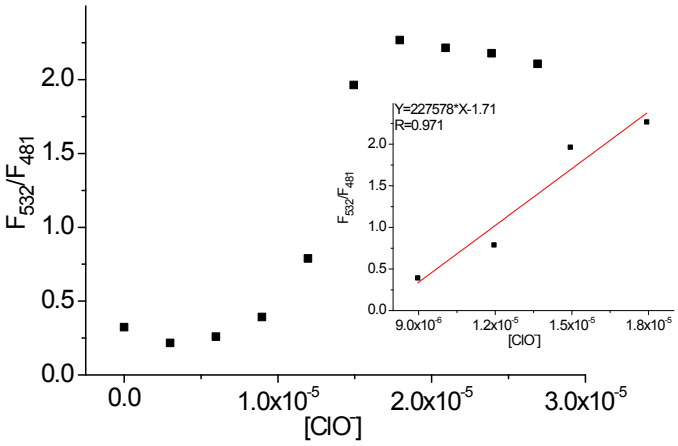


**Figure S9.** Calibration curve of **R1** (0.5 μM) with increasing amount of $ClO^-$ in EtOH/$H_2O$ (4:1, v:v). Inset: linear response range.

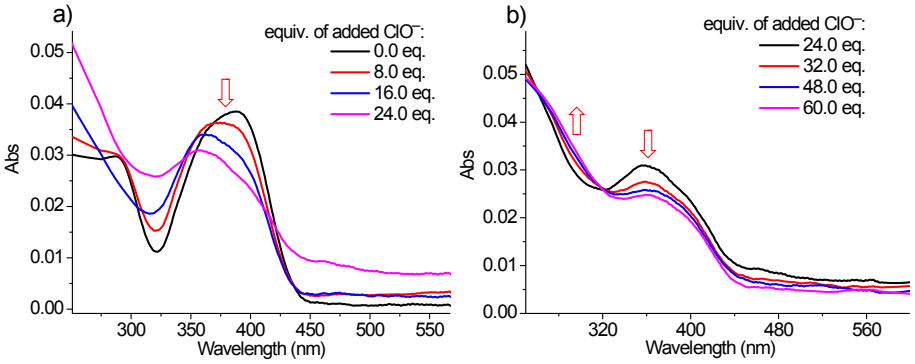


**Figure S10.** UV-visible spectral titration profile of **R1** (1 μM) with an increasing amount of $ClO^-$ (0-60 equiv.) in EtOH/$H_2O$ (4:1, v:v). a) 0-24 equiv. of $ClO^-$; b) 24-60 equiv. of $ClO^-$.

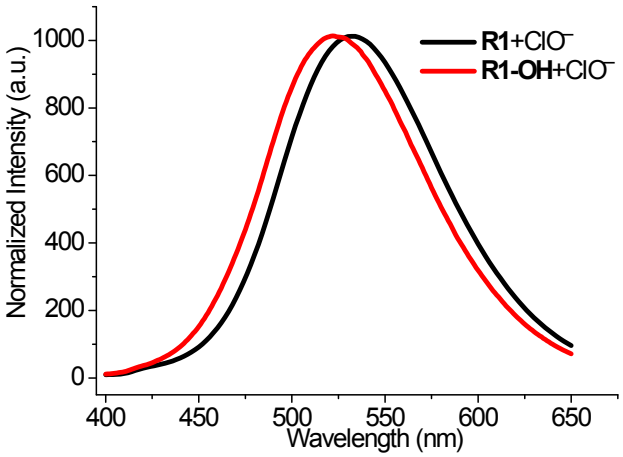


**Figure S11.** Fluorescence spectra (normalized) of **R1**+$ClO^-$ and **R1-OH**+$ClO^-$ in EtOH/$H_2O$ (4:1, v:v).

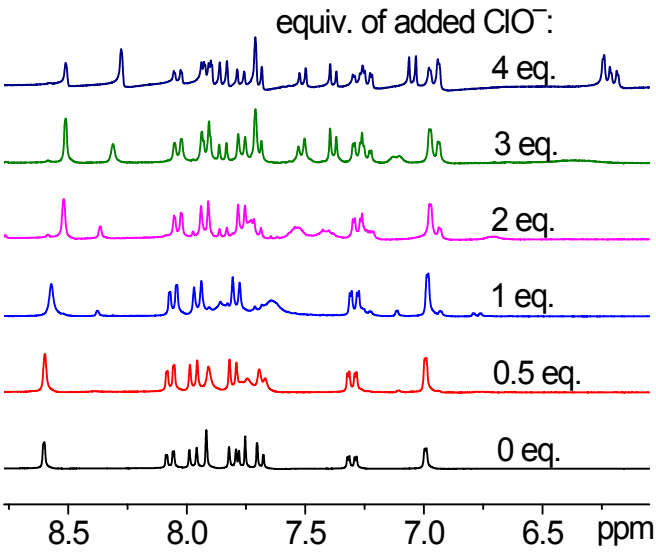


**Figure S12.** Low-field region of the $^{1}$H NMR spectra of **R1** (20 mM) in DMSO-d6 upon successive addition of NaClO solution.

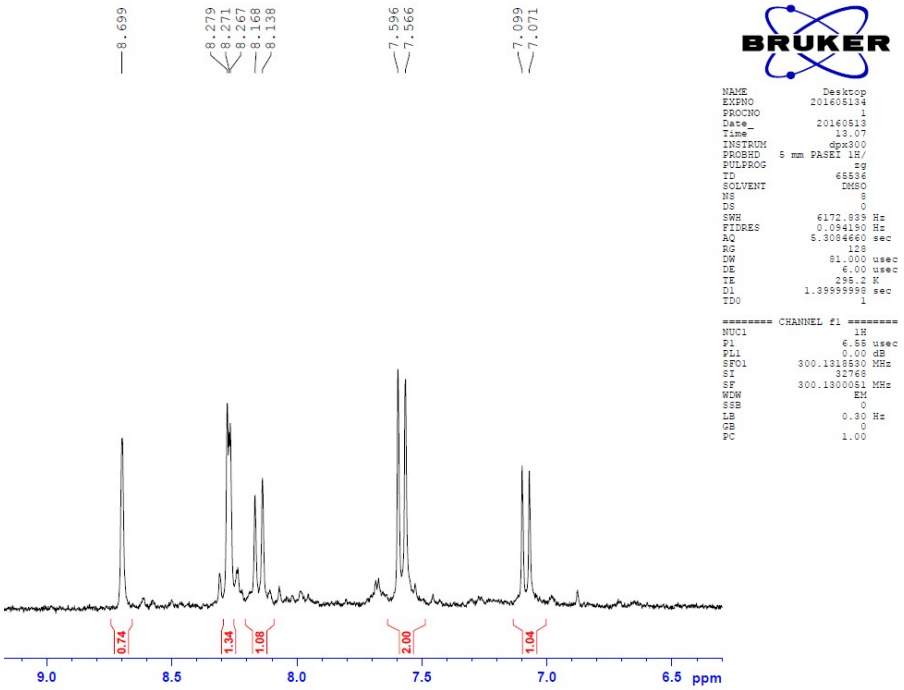


**Figure S13.** Low-field region of the $^{1}$H NMR spectra of the isolated main reaction product of **R1**+$ClO^{-}$ (60 equiv.) in DMSO-d6.

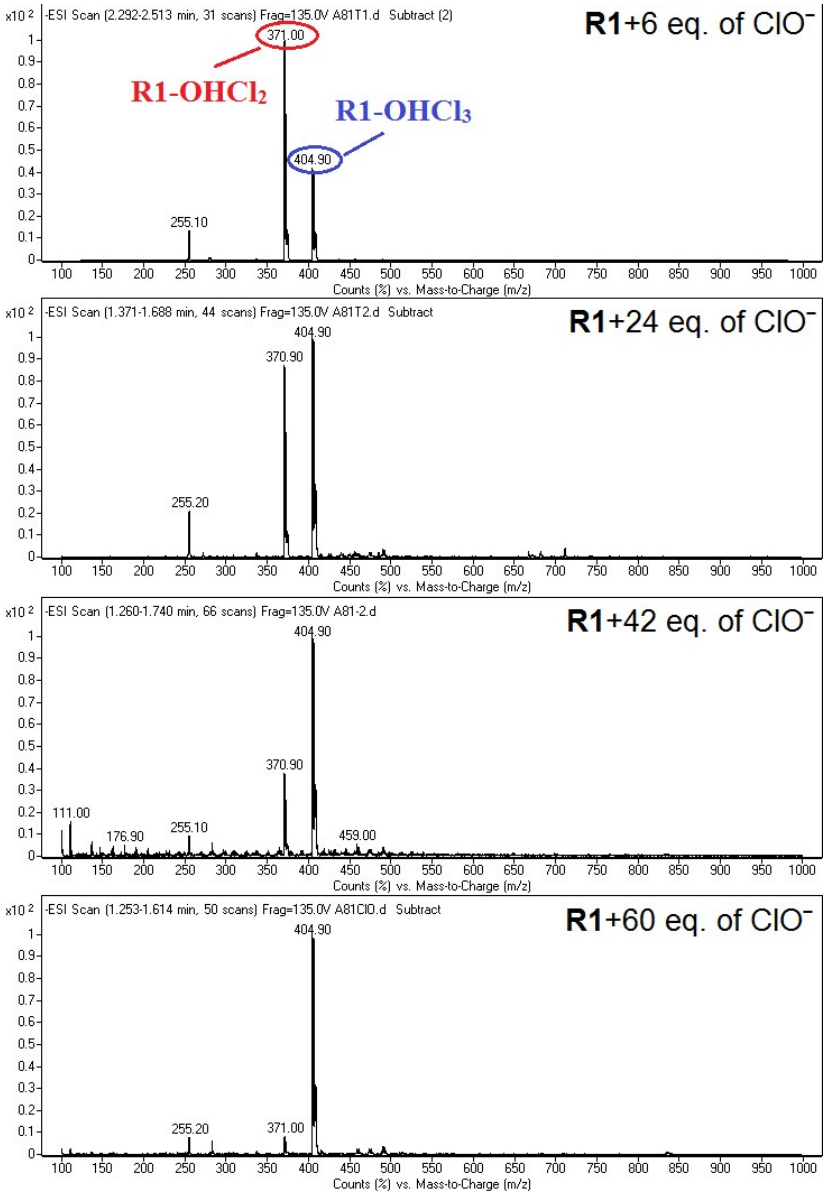


**Figure S14.** MS of the reaction products of **R1**+$ClO^-$. The percentages of **R1-OHCl$_3$** increased with the addition of more equiv. of $ClO^-$.

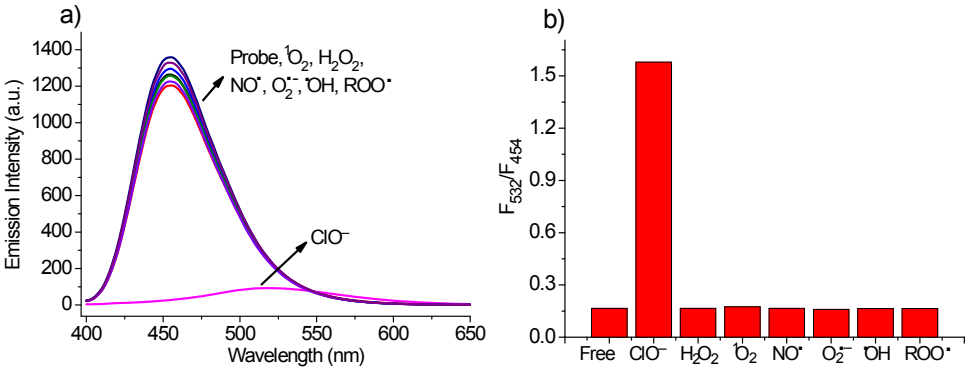


**Figure S15.** Selectivity of **R1-OH** toward $ClO^-$ in EtOH/$H_2O$ (4:1, v:v). a) Emission spectral changes of **R1-OH** (1 μM) after addition of 60 equiv. of various ROS species; b) Corresponding fluorescence intensity ratio of $F_{532}/F_{454}$.

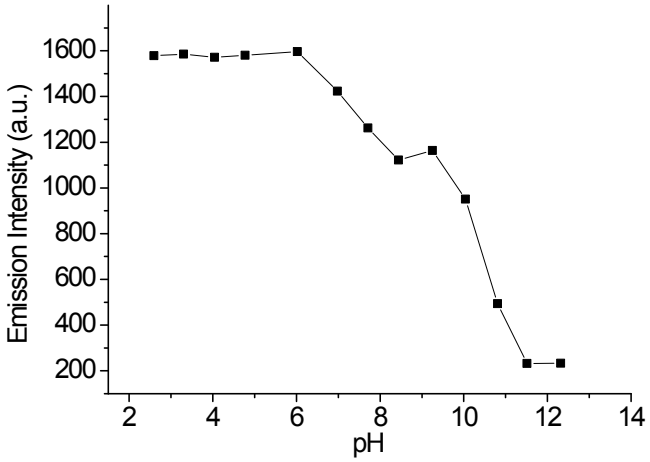


**Figure S16.** Fluorescence emission intensity of **R1-OH** (1 μM) at 454 nm over a pH range of 2.5–12.5.

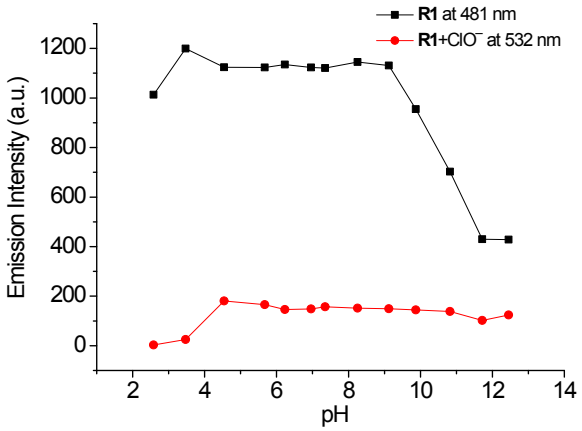


**Figure S17.** Fluorescence emission intensity of **R1** (1 μM, black squares, at 481 nm) and **R1**+$ClO^-$ (60 equiv., red dots, at 532 nm) over a pH range of 2.5–12.5.

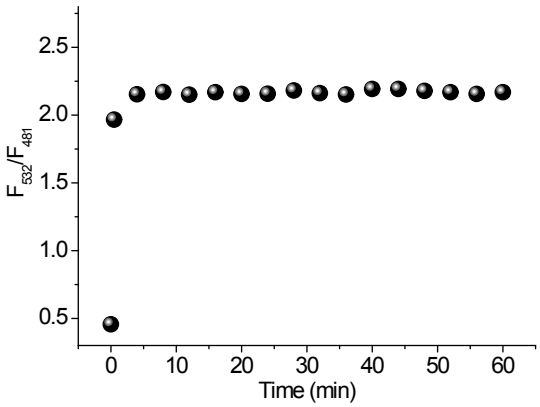


**Figure S18.** Fluorescence intensity ratio of $F_{532}/F_{481}$ of **R1** (1 μM) after addition of 60 equiv. of $ClO^-$ in EtOH/$H_2O$ (4:1, v:v) as a function of time.

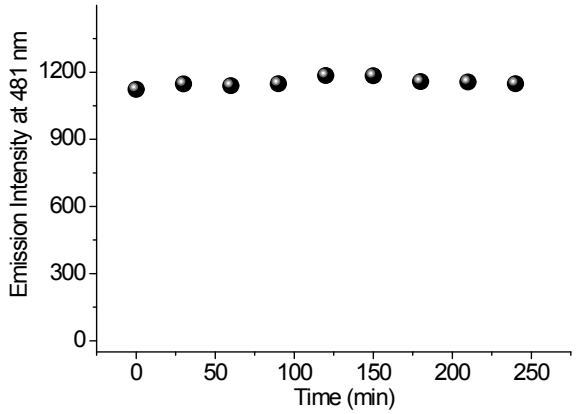


**Figure S19.** Plot shows the fluorescence intensity of **R1** at 481 nm under continuous 365 nm UV light irradiation during 4 h.

**References**


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