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seawater and brine liquor.¹ As a powerful oxidant, HOCl has been used as in the treatment of sewage, the sterilization of hospital laundry, the treatment of cooling water at coastal power stations, and as a bleaching agent in the paper and textile industries. The biochemistry of HOCl promotes the ability of activated phagocytes to kill a wide range of pathogens. It is generated during an oxidation reaction between chloride ions and H₂O₂ that is catalyzed by myeloperoxidase (MPO) secreted by activated phagocytes in the inflammatory state.^{2–5} Although it plays a protective role in human health, excess HOCl can cause tissue damage and diseases such as hepatic ischemia-reperfusion injury, atherosclerosis, lung injury, rheumatoid and cardiovascular diseases, neuron degeneration, arthritis, and cancer.^{6–13} It has been reported that the concentration of HOCl in body fluids under pathological conditions can approach 200 μM. In diseased airways HOCl reaches mM levels.¹⁴

There is thus significant interest in the design of analytical methodologies that target HOCl determination. Instrumental methods include potentiometry, coulometric titration and amperometry.^{15–17} However, many of these methods have relatively high detection limits and require relatively tedious procedures and expensive devices. To address the challenges inherent in the *in vivo* monitoring of HOCl, fluorescent and/or colorimetric indicators based on unique reaction mechanisms have been recently reported by several research groups. These indicator mechanisms include *p*-methoxyphenol oxidation to *p*-benzoquinones,^{18–23} oxime oxidation to aldehydes,^{24–29} the chlorination of thioesters and amides,^{30–40} *p*-aminophenol analog oxidation,^{4,41–44} thioether to sulfonate and selenide to selenoxide transformations,^{5,45–59} the cleavage of carbon-carbon double bonds,^{2,60–62} and oxidative processes in metal complexes.^{7,63–67} This review classifies probes for HOCl based on the seven different detection mechanisms.

1. Oxidation of *p*-methoxyphenol to benzoquinone

It is well-known that *p*-methoxyphenol can be selectively oxidized to benzoquinone by HOCl (Scheme 1). Yang and coworkers were the first to apply the specific reaction between *p*-methoxyphenol and HOCl towards both the detection of HOCl as well as its bioimaging.¹⁸

As shown in Fig. 1, HOCl oxidizes the PET-quenched BODIPY-type probe **1** to the corresponding quinone. This resulted in strong emission at 541 nm when excited at 520 over a pH range of 5–7.5. The probe was successfully employed to image the production of HOCl in live macrophage cells. The probe enabled detection of HOCl without interference from related oxidizing agents including H₂O₂, ¹O₂, •NO, O₂•[–], •OH, ONOO[–], and ROO•. For a continuous work, the Yang group recently reported a series of second generation probes (**2a**, **2b**, and **2c**) with enhanced selectivity, sensitivity, and chemostability.¹⁹ Further, probe **2b** could be used for endogenous HOCl Visualization in both RAW264.7 mouse macrophages and human THP-1 monocytic macrophages.

A highly selective naked-eye probe, *p*-methoxyphenol-substituted aniline derivative **3**, for the detection of ClO[–] in aqueous solutions in the pH range of 5–9, was recently reported.²⁰ Upon the addition of ClO[–] in PBS to **3**, a decrease in the absorption band at 310 nm and formation of a new bathochromic absorption band with a maximum at 572 nm was detected. This new absorption was attributed to the oxidation of the *p*-methoxyphenol unit to the

corresponding benzoquinone-substituted aniline which resulted in the colorless solution turning blue gradually via an ICT process (Fig. 2). The detection limit was estimated at 1.74 μM . In the presence of other reactive oxygen and nitrogen species including H_2O_2 , $^1\text{O}_2$, $\cdot\text{NO}$, $\text{O}_2^{\cdot-}$, $\cdot\text{OH}$, ONOO^- and $\text{ROO}\cdot$, the absorption spectrum of **3** remained relatively unaltered. The presence of both anions (*i.e.*, F^- , Cl^- , Br^- , I^- , ClO_3^- , ClO_4^- , CO_3^{2-} , SO_4^{2-} , PO_4^{3-} , H_2PO_4^- and OH^-) and cations (*i.e.*, Fe^{2+} , Fe^{3+} , Cu^{2+} and Zn^{2+}) did not interfere with the visible detection of ClO^- .

Yang and co-workers designed and synthesized a simple, water-soluble *p*-methoxyphenol derivative **4** that shows colorimetric and fluorimetric dual-signaling responses for HOCl in PBS buffer (0.01 M, pH 7.4) (Fig. 3).²¹ In the presence of ClO^- , the solution color changed as a result of the shift of the original absorbance of **4** at 314 nm to 393 nm. Fluorescence emission 388 nm decreased dramatically upon increasing ClO^- concentration. The observed behavior was attributed to *p*-methoxyphenol oxidation. The addition of other reactive oxygen and nitrogen species (H_2O_2 , $^1\text{O}_2$, $\cdot\text{NO}$, $\text{O}_2^{\cdot-}$, $\cdot\text{OH}$, ONOO^- and $\text{ROO}\cdot$) did not induce signaling.

A water-soluble dihydrofluorescein-ether probe **5**, was also designed on the basis of a similar HOCl-promoted oxidation (Fig. 4).²² Upon addition of HOCl a > 1000-fold fluorescence enhancement at 485 nm after 30 min in HEPES buffer (20 mM, pH 7.2) was observed. The presence of other oxidizing species showed negligible fluorescent enhancement, even at 1000 equiv. levels compared to probe concentration. The detection limit was estimated to be 6.68 nM on the basis of the signal-to-noise ratio ($S/N=3$). Live cell imaging studies showed that **5** possessed excellent cell membrane permeability and non-cytotoxic properties.

Yin and co-workers reported a curcumin-based fluorescent probe **6** for the detection of HOCl in biological systems (Fig. 5).²³ When excited at 420 nm, the addition of HOCl to **6** in MeOH:HEPES (pH 7.0) 3:1 (*v/v*) caused a fluorescent decrease at 544 nm. Excellent selectivity for HOCl was observed compared to other oxidants. A detection limit of 0.065 μM was reported. Probe **6** functioned over the pH range of 7–11, thereby rendering it potentially useful for environmental or industrial applications. The probe was cell permeable and detected HOCl in 84 disinfectant samples.

2. The oxidative deoximation reaction of luminescent oxime

Hydroxylamines are converted to aldehydes via a deprotection reaction with ClO^- under mild conditions (Scheme 2).²⁴ There are several examples whereby fluorescence intensity has been enhanced by the removal of a C=N bond in a fluorogenic molecule via the reaction of an oxime and HOCl.^{27–29}

The oxime based probe **7** was first employed as a probe for HOCl by Lin (Fig. 6).²⁴ Through an ICT process, **7** exhibits strong blue fluorescent emission at 439 nm when excited at 394 nm in phosphate buffer (0.1 M, pH 9.0):DMF 1:4 (*v/v*). When the reaction occurs, the stronger ICT of the product induces a red shift of about 70 nm. Additionally, the varying the pH in the aqueous portion from 2.5 to 10.5 showed a negligible effect on the ratiometric

responses of 7 to ClO^- . A wide variety of cations, anions and oxidants were tested for potential interference but did not affect the detection of HOCl.

An oxime-based turn-off chemosensor **8** for HOCl was designed by the Li group (Fig. 7).²⁵ Triphenylamine derivative **8** showed strong blue fluorescence centered at 458 nm when excited at 339 nm in phosphate buffer (0.1 M, pH 9):DMF 1:4 (v/v) at rt. Upon addition of HOCl, a dramatic fluorescent decrease could be visually observed by the naked eye in a room under normal lighting that quenched when the concentration of HOCl reached 200 equiv. The process completed in 3 min. A linear correlation was observed between the emission intensity and the concentration of ClO^- over a range of 7 to 18×10^{-5} M. The probe functioned at pH values 8.0 and 10.0. The presence of excess levels of other analytes, including Li^+ , ClO_4^- , H_2O_2 , Na^+ , NO_2^- , Cu^{2+} , Cl^- , OAc^- , K^+ , ClO_3^- , CO_3^{2-} , SO_4^{2-} , Zn^{2+} , and Mg^{2+} did not effect HOCl-induced signaling.

Two more oxime-based colorimetric probes for ClO^- have been reported (Fig. 8).²⁶ In solutions of **9a** and **9b**, the reaction caused a change in their UV-vis spectra via ICT. **9a** shows maximum absorption at 453 nm with a molar extinction coefficient (ϵ) of $2.1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ in phosphate buffer (0.1 M, pH 9.2):DMF 4:1, (v/v) at rt. Upon the introduction of ClO^- (32 equiv.) to the solution of **9a** (10 μM), the absorption maximum of **9a** shifts from 453 to 475 nm. Because of the presence of the nitro group in **9b**, the absorption spectrum of **9b** shows a bathochromic-shift band centered at 489 nm. Upon addition of ClO^- , the absorption of **9b**, centered at 489 nm, gradually decreased with concomitant formation of a new peak at 510 nm, corresponding to a color change from orange to pink, which was clearly visible. The detection limit of **9b** for ClO^- was 2 μM . Similar to other HOCl probes, **9a** and **9b** show high selectivity for ClO^- over other cations, anions and oxidants.

A novel iridium (III) complex of an oximated 2,2'-bipyridine based ClO^- probe was reported by the Chen group (see Fig. 9).²⁷ Complex **10** is almost non-emissive due to C=N-OH isomerization as a predominant non-radiative decay process in the excited state. Through the selective oxidation of the oxime to an aldehyde or carboxylic acid, the addition of ClO^- caused strong fluorescent emission at 578 nm when excited at 346 nm in DMF:HEPES (50 mM, pH 7.2) 4:1 (v/v). DFT computational studies revealed that the produced complex $[\text{Ir}(\text{ppy})_2(\text{L2})](\text{PF}_6)$ exhibits bright orange-yellow luminescence originating from $[5d(\text{Ir}) \rightarrow \pi^*(\text{bpy})]$ $^3\text{MLCT}$ and $[\pi(\text{ppy}) \rightarrow \pi^*(\text{bpy})]$ $^3\text{LLCT}$ triplet excited states, which were comparable to those of the experimental data. The selectivity of probe **10** toward ClO^- was shown to be unaffected by the presence of H_2O_2 , $\cdot\text{NO}$, $\text{O}_2^{\cdot-}$, $\cdot\text{OH}$, $\text{ROO}^{\cdot}$ and various metal ions. In addition, the use of test strips containing **10** showed highly promising sensitivity to ClO^- .

A “turn-on” fluorescent probe (**11**) for HOCl based on a fluorescein-oxime architecture was synthesized (Fig. 10).²⁸ Along with the specific oxidation reaction of the oxime and HOCl, reaction induced distinct fluorescent emission at 530 nm when excited at 454 nm in DMSO:HEPES (10 mM, pH 7.05) 1:9 (v/v). The solution color changes from colorless to light yellow which could be readily visualized. The emission at 530 nm increased gradually upon increasing the concentration of ClO^- . The detection limit was 5 μM . Selectivity studies showed that AcO^- , NO_2^- , NO_3^- , ClO_3^- , F^- , ClO_4^- , HCO_3^- , PO_4^{3-} , Cl^- , IO_3^- , HPO_4^{2-} ,

Br^- , HSO_3^- , HSO_4^- , I^- , $\text{S}_2\text{O}_3^{2-}$, SCN^- , and H_2O_2 did not interfere with ClO^- analysis. Probe **11** could thus be potentially used in sensing and cellular imaging.

A BODIPY-based turn-on fluorescent probe **12** was designed and synthesized for the fluorescence detection of ClO^- in aqueous media (Fig. 11).²⁹ Probe **12** exhibits poor fluorescence. Upon addition of HOCl, a band appears at 525 nm when excited at 500 nm in PBS buffer (0.1 M pH 7.4). The fluorescence intensity versus ClO^- concentration plot is linear over a range from 0 to 6 mM. The detection limit was determined to be 17.7 nM. Other potentially competing reactive oxygen species (ROS) or reactive nitrogen species (RNS) did not affect the detection of HOCl. Probe **12** is reported to be fast-responding, highly sensitive, photostable and water soluble. Its utility was demonstrated in imaging both exogenous and endogenous ClO^- in live cells.

3. The chlorination of thioesters and amides by HOCl

As a strong oxidant, HOCl can react with thioesters and amides via chlorination reactions to produce $-\text{S}-\text{Cl}$ and $-\text{N}-\text{Cl}$ species as intermediates (Scheme 3). These intermediates lead to carboxylates in aqueous solution. When a hydrazide group is a component of the sensing system, the chlorination reaction converts the hydrazine moiety to azo. The design of probes containing fluorophores with the aforementioned functional groups has led to several unique HOCl indicators.

Loo, Zhang and co-workers reported a novel water-soluble organic-nano up-conversion luminescence (UCL) detection system for HOCl based on a rhodamine-modified thiosemicarbazide (**13**, Fig. 12).³⁰ Upon reaction of **13** with HOCl, the green UCL emission intensity gradually decreased as near-infrared (NIR) emission exhibited no change, a desirable property for ratiometric UCL detection. The nanoparticles were successfully used for ratiometric UCL visualization of HOCl that was released by MPO-mediated peroxidation of chloride ions in living cells.

Very recently the Yuan group synthesized a ruthenium-ferrocene (RuFc) multisignal chemosensor for the highly selective detection of lysosomal HOCl (Fig. 13).³¹ Probe **14** was weakly luminescent because MLCT (metal-to-ligand charge transfer) state was hindered by an efficient PET (photoinduced electron transfer) process from the Fc moiety to the Ru(II) center. The cleavage of the Fc moiety occurred via a HOCl-induced oxidation of a hydrazide-derived linker, resulting in elimination of PET, accompanied by striking photoluminescence (PL) and electrochemiluminescence (ECL) enhancements. Probe **14** exhibited low cytotoxicity and was used for the quantitative detection of HOCl in live cells by confocal microscopy imaging and flow cytometry analysis. The imaging of endogenous HOCl generated in live macrophage cells during the stimulation was achieved. HOCl was visualized in laboratory model animals, *Daphnia magna* and zebrafish.

Wu and co-workers reported a BODIPY-based fluorescent probe for the detection of HOCl based on a hypochlorous acid-promoted oxidative intramolecular cyclization (Fig. 14).³² The reaction was accompanied by a 41-fold increase in the fluorescent quantum yield (0.004 to 0.164) and fluorescence intensity was linear in the HOCl concentration range of 1–8 μM

with a detection limit of 2.4 nM ($S/N = 3$). Confocal fluorescence microscopy imaging using RAW264.7 cells showed that probe **15** was effective in living cells.

The Ma group used an *N*-benzoyl rhodamine B-hydrazide **16** (Fig. 15) for HOCl detection.³³ Probe **16** has no absorption in the visible region in its closed spirolactam form. Upon reaction with ClO^- , however, a new absorption band at 556 nm appeared as the solution color changed from colorless to pink. The reaction thus restored the rhodamine B color as a function of increasing ClO^- concentration. Similarly, rhodamine fluorescence ($\lambda_{\text{em}} = 578 \text{ nm}$) was observed in $\text{Na}_2\text{B}_4\text{O}_7$ buffer (0.03 M, pH 12):THF 7:3 (v/v). The turn-on probe exhibited $F = 52.69C - 29.83$ ($n = 10$, $\gamma = 0.9992$) and a detection limit of 27 nM ($S/N = 3$). Further selectivity experiments displayed high selectivity of probe **16** to ClO^- over other species including Ca^{2+} , Cu^{2+} , Fe^{3+} , Fe^{2+} , Hg^{2+} , K^+ , Mg^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} , MnO_4^- , H_2O_2 , Cl^- , ClO_3^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , and SiO_3^{2-} .

A new fluorescent probe **17** for HOCl was synthesized from rhodamine 6G based on its chlorination reaction (Fig. 16).³⁴ Fluorescence intensity changes of probe **17** towards HOCl (5.0 equiv.) and other ROS (100 equiv. of H_2O_2 , $\cdot\text{NO}$, $\text{O}_2^{\cdot-}$, $\cdot\text{OH}$, $\text{ROO}\cdot$) in PBS buffer (pH 7.4):DMF 999:1 (v/v) were measured to evaluate the selectivity of **17**. Only HOCl enhanced the fluorescence intensity at 547 nm when excited at 500 nm to a significant extent. The other ROS studied did not interfere. In addition to the fluorescent changes, the solution changed from colorless to pink as readily observed by visual inspection. Fluorescence titration of **17** with HOCl afforded a limit of detection of 25 nM. In cellular experiments, probe **17** showed favorable membrane permeability and was used in the bioimaging of HOCl.

Subsequently, a rhodamine B thiospirolactone-based probe **18** was successfully developed as a highly sensitive and selective fluorescent probe for HOCl by Xu's team (Fig. 17).³⁵ In this investigation, both the absorption and fluorescence spectra of the probe, as a function of varying concentration of NaClO, were measured in phosphate buffer (0.1 M, pH 7.4):DMSO 99:1 (v/v). The probe solution without added NaClO was colorless and non-fluorescent, due to the spiro-ring structure. Dramatic formation of a pink solution color observed upon addition of NaClO, accompanied by significant enhancements in absorption (561 nm) and fluorescence (579 nm, excited at 525 nm). The probe afforded a linear correlation between the emission intensity and NaClO (0.5–7.0 μM) concentration, with a detection limit of 0.3 μM . Probe **18** overall exhibited high selectivity, function over a wide pH range, and favorable photostability and toxicity profiles, thereby showing great potential for bioimaging and environmental detection.

An analogous fluorescent probe **19** for HOCl based on rhodamine 19 was later reported by the Yoon group (Fig. 18).³⁶ Initially, treatment of **19** with 1 equiv. HOCl resulted in a significant fluorescence increase at 547 nm in phosphate buffer (0.1 M, pH 5.5): CH_3CN 99:1 (v/v). Probe **19** displayed high selectivity toward HOCl over excess (20 equiv.) other ROS, such as H_2O_2 , $^1\text{O}_2$, $\cdot\text{NO}$, $\text{O}_2^{\cdot-}$, $\cdot\text{OH}$, ONOO^- and $\text{ROO}\cdot$. Fluorescent titration experiments demonstrated that the fluorescence intensity of **19** and HOCl concentration had a linear relationship over a HOCl concentration range of 0–12 μM . Impressively, the high specificity and sensitivity of **19** as well as its unique activity under relatively acidic

conditions rendered it useful towards visualizing phagosomal and mucosal HOCl production in a variety of cellular contexts. This successful application of HOCl detection and imaging in live cells and tissues of an animal model should inspire investigations of the role of HOCl in a wide variety of biological processes.

A water-soluble fluorescence resonance energy transfer (FRET) probe **20** for HOCl was designed, synthesized and characterized (Fig. 19).³⁷ Probe **20**, connects a FRET donor (dansyl, DNS) and FRET acceptor (rhodamine, RBPH) via a HOCl-cleavable active bond. It was found to react with HOCl and afford a change of fluorescence at pH = 7.4. Through intramolecular FRET, the fluorescence of the DNS unit of **20** is quenched, and only the fluorescence ($\lambda_{em} = 585$ nm) of the RBPH unit is observed ($\Phi = 0.07$ in H₂O). When HOCl was added to the probe solution, the DNS fluorescence ($\lambda_{em} = 501$ nm) appeared and, surprisingly, the fluorescence intensity of the RBPH unit also increased ($\Phi = 0.19$ in H₂O). In the titration experiment, the plot of fluorescence intensities of **20** at 501 nm showed a linear relationship to the concentration of HOCl over a 2–10 μ M range, with a regression equation of $F = 0.704C + 0.097$ and a linear correlation coefficient of 0.998. The detection limit was 80 nM ($S/N = 3$). Based on its solubility and sensitivity, probe **20** was successfully used in the fluorescence imaging of HOCl in HeLa cells.

Another rhodamine 6G-based fluorescent probe **21** for the detection of HOCl, functioning over a wide pH range, was reported by the Zeng group (Fig. 20).³⁸ Upon addition of various anions and metal cations, such as Cl⁻, ClO₄⁻, NO₂⁻, NO₃⁻, SO₄²⁻, ClO⁻, Ca²⁺, K⁺, Mg²⁺, Pb²⁺, Ni²⁺, Zn²⁺, Fe³⁺, Cu²⁺, Hg²⁺ and H₂O₂ to a solution of **21** in H₂O, only HOCl induced a new absorption band centered at 521 nm. The fluorescence titration profiles of solutions of **21** with added NaClO were measured upon excitation at 505 nm and emission at 548 nm in H₂O. Addition of HOCl to **21** induced fluorescent enhancement at 548 nm over a wide pH range (pH = 6–12). In addition, the oxidation product of **21** was stable over a wide pH range. These findings suggest that artificial buffer solutions are not required for the detection of ClO⁻. Moreover, probe **21** could be used in the detection of ClO⁻ in both running tap water and earth-soaked water.

Based on the specific chlorination reaction, two fluorescein-based probes, **22a** and **22b** (Fig. 21), were designed for the detection of HOCl.³⁹ Similar to the rhodamine derivatives, their chlorination products exhibited excellent photophysical properties via the ring-opened structure. The addition of HOCl to **22a** and **22b** (pH = 7.4) induced strong green fluorescence emission at 528 nm for **22a** and at 527 nm for **22b** with excitation at 480 nm. In contrast, other species such as NaCl, KCl, CaCl₂, Mg(ClO₄)₂, Fe(ClO₄)₂, Zn(ClO₄)₂, Cu(ClO₄)₂, Hg(ClO₄)₂ and H₂O₂ did not induce any fluorescent enhancement for **22a**. For **22b**; however, a fluorescence enhancement at 530 nm was also observed in the presence of Hg²⁺, though other analytes did not interfere.

Recently, Yoon *et al.* reported a “dual-lock” fluorescein based HOCl probe **23** (Fig. 22).⁴⁰ In this investigation, both FBS (**23**) and FS were studied for their potential fluorescent responses to various ROS/RNS. Only HOCl could both react with the arylboronates as well as hydrolyze the thiolactone to afford the fluorescein. Probe **23** was successfully applied to the *in vivo* imaging of physiological HOCl production in the mucosa of live animal models.

4. Oxidation reactions of *p*-aminophenol analogues

Like *p*-methoxyphenol, the *p*-aminophenyl aryl ether moiety reacts expeditiously with ROS, and preferably with ClO^- , to give 1,4-benzoquinone imines via an *ipso*-substitution mechanism (Scheme 4).⁴¹ The utility of this moiety for designing HOCl-selective indicators is described in the following examples.

The Libby group designed and synthesized sulfonaphthoaminophenyl fluorescein **24** as a HOCl probe based on the reaction of the *p*-aminophenyl aryl ether moiety with HOCl (Fig. 23).⁴ Upon addition of HOCl to a solution of **24** (pH 7.4), a strong fluorescence signal was generated at 676 nm upon excitation at 614 nm. Other reactive oxygen and nitrogen species, including H_2O_2 , $\cdot\text{NO}$, $\text{O}_2^{\cdot-}$, $\cdot\text{OH}$, and $\text{ROO}^\cdot$, did not interfere with the detection of HOCl at concentrations up to 10 equiv. The *in vivo* imaging of HOCl, produced by neutrophils in experimental murine peritonitis and MPO expressing cells in human atherosclerotic arteries, was successfully achieved via probe **24**. Probe **24** may thus embody provide a valuable non-invasive molecular imaging tool for implicating HOCl and MPO in the damage of inflamed tissues.

Two lanthanide complex-based luminescent probes, **25a** and **25b** (Fig. 24), were designed and synthesized for highly sensitive and selective time-gated luminescence detection of HOCl in aqueous media.⁴² The probes were nearly non-luminescent due to the PET interaction between the 4-amino-3-nitrophenyl moiety and the terpyridine- Ln^{3+} moiety, which quenched the lanthanide luminescence. Upon addition of HOCl, the 4-amino-3-nitrophenyl moiety was rapidly cleaved from the probe complexes, which afforded strongly luminescent lanthanide complexes HTTA- Eu^{3+} and HTTA- Tb^{3+} , exhibiting luminescence enhancements at 610 nm and 540 nm respectively.

Nabeshima and Lu used the HOCl-promoted cleavage of the PET quenching 4-amino-3-nitrophenyloxy moiety of a weakly emissive iridium complex (**26**) to afford a highly luminescent complex that is highly selective for HOCl and was shown to successfully image HOCl in HeLa cells (Fig. 25).⁴³

The Qian group designed and synthesized the highly water soluble fluorescence probe **27** (Fig. 26).⁴⁴ With no fluorescence responses over a pH range from 6.5 to 11.0, probe **27** is suitable for applications under physiological conditions. Upon addition of ClO^- , **27** showed a dual-channel emission at 460 nm and 570 nm, with excitation at 340 nm in phosphate buffer (0.1 M, pH 7.4):DMF 99:1 (v/v). In contrast, OONO^- led to a single-channel enhancement at 460 nm only and other ROS/RNS induced no spectral changes. As **27** can distinguish ClO^- from ROS/RNS via its dual-channel signal, it was successfully used to image ClO^- in live HeLa cells.

5. Thioether to sulfonate and selenide to selenoxide

Thioethers and selenides are electron donating groups that are easily oxidized by HOCl to produce sulphonates and selenoxides, which are strong electron withdrawing groups (Scheme 5). The process enables thioether- or selenide-containing probes to display useful signal changes either in their fluorescence or UV-vis spectra upon reacting with HOCl.

On the basis of the specific oxidation reactions, Nagano and coworkers developed a novel fluorescence probe selective for HOCl. Their strategy involved tuning the nucleophile affecting the spirocyclization of tetramethylrhodamine derivatives (Fig. 27), resulting in the creation of thioether **28**.⁴⁵ Upon addition of HOCl, **28** shows rapid and quantitative emission at 575 nm at pH in phosphate buffer (0.1 M, pH 7.4):DMF 999:1 (v/v). Additionally, **28** displayed excellent stability in the presence of various abundant ROS generated in organisms under physiological conditions. With excellent properties at varying pH, including high photo- and oxidative stability, **28** has potential as a useful fluorescence probe for biological phenomena, such as phagocytosis.

Motivated by the aforementioned results, Nagano's team modified probe **28** in the synthesis of two Si-rhodamine far red emitting fluorescent probes **29a** and **29b** (Fig. 28).⁵ For both **29a** and **29b**, the absorption and maxima were close to 650 nm. Upon the addition of various ROS, only HOCl promoted emission at 670 nm (pH 7.4, 0.1% DMF), with good sensitivity. Furthermore, cellular and whole animal experiments suggested that the use of **29** was applicable to *in vitro* and *in vivo* imaging.

The Chang group employed a dithiolane-protected pyrene-aldehyde, as HOCl probe **30** (Fig. 29), which displayed both colorimetric and turn-on fluorescent responses.⁴⁶ The UV-vis spectrum of **30** showed strong absorption bands at 315, 329, and 345 nm in 50% aqueous CH₃CN. Upon treatment of **30** with 10 equiv. HOCl, the dithiolane group was removed, and new absorption bands at 361 and 395 nm appeared along with strong emission at 457 nm. Hg²⁺ could induce the same dithiolane deprotection as HOCl, which could be readily circumvented by employing a Chelex-100 resin.

The Chang group recently incorporated the dithiolane strategy to create a series of two-photon fluorescent "turn-on" HOCl probes, including mitochondria- and lysosome-targeting derivatives, which imaged intracellular HOCl in live cell and inflamed mouse models (Fig. 30).⁴⁷

Gold nanoparticles (Au NPs) are widely used as ligating atoms in coordination and nanochemistry, and readily interact with thiols to afford colorimetric responses. A sulfhydryl ligand can be oxidized by ClO⁻ to a sulfonate, thereby desorbing the ligand. Probe **32** (Fig. 31) was designed as a colorimetric probe based on this process.⁴⁸ Upon the addition of ClO⁻, the UV-vis absorption of Au NPs-**32** at 527 nm decreased gradually as a new peak at 680 nm increased, as the solution color changed from blue to red. Moreover, several environmentally relevant anions and cations including Cl⁻, NO₃⁻, SO₄²⁻, CO₃²⁻, Ca²⁺, Mg²⁺, Fe³⁺, Al³⁺, Cu²⁺, and Zn²⁺ were evaluated as possible interferents in ClO⁻ detection. Metal cations at < 0.1 mM levels and all anions studied did not affect the HOCl detection process. Tap water experiments demonstrated the applicability of probe **32** for the detection of ClO⁻ in real-world environmental samples.

A novel silica nanoparticle probe (**33**) comprising FITC (donor dye) and a non-fluorescent chemodosimeter rhodamine (acceptor dye) was designed and synthesized for HOCl detection via a FRET mechanism (Fig. 32).⁴⁹ Triggered by HOCl, as shown in Fig. 32, the rhodamine moiety "T" became fluorescent via a tandem oxidation and β -elimination to

produce “III”. Via the FRET interaction between the fluorescein donor and the newly formed rhodamine acceptor, the ratio of the fluorescence intensities ($I_{586\text{ nm}}/I_{526\text{ nm}}$) increased significantly, enabling determination of HOCl concentration. The nano dosimeter was used for ratiometric reporting of HOCl levels in lysosomes in live cells. It functions over a wide pH range and appears to be relatively non-cytotoxic.

A dithiothreitol fabricated gold nanoparticle (AuNP) probe **34** was developed for the facile colorimetric detection of ClO^- .⁵⁰ Owing to the strong covalent S-Au bond, dithiothreitol causes AuNPs to aggregate resulting in a color change from red to blue (Fig. 33). In the presence of ClO^- , however, the thiol groups are oxidized, reforming the red solution. Using this colorimetric method, 2 μM of ClO^- was readily seen by visual inspection within 5 min. The method was successfully applied to ClO^- determination in water samples.

A fascinating Si-fluorescein based fluorescent probe **35** was synthesized by the McCarroll group (Fig. 34).⁵¹ Through the specific oxidation reaction of **35** and 1 equiv. HOCl, two open-form Si-fluorescein analogues **35-I** and **35-II** were produced. As shown in Fig. 34, in the absence of HOCl, the solutions are colorless and non-fluorescent. The addition of HOCl resulted in a new peak at 586 nm in the UV-vis spectrum in PBS (pH 7.4):DMF 199:1 (v/v) (Fig. 34, A). Excitation at this wavelength results in a strong fluorescence band centered at 606 nm (Fig. 34, B). However, both the absorption and fluorescence responses of the two products were pH dependent. Specifically, the λ_{586} band began to decrease, while a new relatively broad band at 475 nm increased as the pH of the buffer solution decreased (Fig. 34, C). The corresponding fluorescence spectra of these solutions show that the probe's fluorescence intensity decreases under increasingly acidic conditions (Fig. 34, D). The fluorescence and UV-vis intensities and the ratio between the λ_{586} and the λ_{475} bands could be used to indicate the concentration of HOCl and the pH of the solution simultaneously. An excess amount of HOCl (around 5 equiv.) causes chlorination and further induces a red shift. This feature increased the detection range to 0–80 equiv. of HOCl.

A novel Ru (II) complex, **36**, was designed and synthesized as a highly sensitive and selective luminescence probe for the recognition and detection of HOCl in living cells by exploiting a “signaling moiety-recognition linker quencher” sandwich approach (Fig. 35).⁵² Owing to the effective PET from the Ru (II) center to the electron acceptor, 2,4-dinitrophenyl, the probe itself was non-fluorescent. In aqueous media, HOCl triggered the oxidation reaction to cleave the 2,4-dinitrophenyl moiety from **36**, resulting in the formation of a highly luminescent bipyridine-Ru(II) complex derivative, accompanied by a 190-fold luminescence enhancement at 626 nm with excitation at 450 nm. Cell imaging results demonstrated that **36** was membrane permeable, and could be applied to visualizing the exogenous/endogenous HOCl molecules in living cell samples.

The Wu group developed a boron dipyrromethene (BODIPY)-based fluorimetric probe, **37**, for the highly sensitive and selective detection of HOCl (Fig. 36).⁵³ Confirmed by ^1H , ^{13}C NMR spectroscopy and mass spectrometry, the methyl phenyl sulfide moiety of **37** was oxidized by HOCl to produce sulfoxide, which eliminated the electron donor and further interdicted the PET process, accompanied by a 160-fold increase in the fluorescent emission at 516 nm with excitation at 505 nm in PBS (0.1 M, pH 7.4): CH_3CN 99:1 (v/v). The

fluorescence intensity of HOCl and **37** showed good linearity in the HOCl concentration range 1–10 μ M. A detection limit of 23.7 nM ($S/N=3$) was determined. In addition, confocal fluorescence microscopy imaging of RAW264.7 macrophages demonstrates that **37** could be an efficient optical detector of HOCl in living cells.

Another BODIPY-based fluorescent probe **38**, bearing an organoselenium group, was synthesized for HOCl detection by the Wu group (Fig. 37).⁵⁴ Compound **38** was oxidized to the selenoxide by HOCl, as confirmed by ⁷⁷Se NMR and MS spectra. Probe **38** displayed weak fluorescence with a quantum yield of $\Phi = 0.005$. Upon the addition of HOCl, the strong fluorescence of BODIPY centered at 526 nm was restored with a quantum yield of $\Phi = 0.690$ with excitation at 510 nm in PBS (0.1 M, pH 7.4):CH₃CN 99:1 (v/v). Probe **38** exhibited high selectivity and sensitivity toward HOCl over other ROS and RNS in aqueous solution. Furthermore, the detection limit was as low as 7.98 nM. Importantly, **38** showed good cell membrane permeability and could be successfully applied to image endogenous HOCl in living cells.

A reversible fluorescent probe **39**, which connected 1,8-naphthalimide as a signal transducer and diphenyl-selenide as the reaction site, was synthesized and characterized (Fig. 38).⁵⁵ A proposed PET process was validated by time-dependent density functional theory (TD-DFT) calculations. In addition, the influence of viscosity and temperature demonstrated that there was an excited state configuration twist process, which would lead to fluorescence quenching in **39**, but not in the selenoxide product. The addition of HOCl caused strong fluorescent emission at 523 nm in phosphate buffer (20 mM, pH 7.4). In the inverse process, the addition of thiols could cause a decrease of the fluorescence intensity via reduction of selenoxide. Importantly, using confocal fluorescence microscopy, **39** enabled visualization of HOCl and reducing repair in live cells and live mice *in situ*.

The Jiang group developed a new strategy for HOCl selective fluorescent probes **40a** and **40b** based on the selenoxide elimination reaction (Fig. 39). The selenoxide elimination has been used in organic synthesis to prepare α,β -unsaturated esters and ketones, olefins and allyl alcohols under mild conditions (Fig. 39).⁵⁶ The probes **40a** and **40b** display no major absorption bands or fluorescence emission ($\Phi < 0.001$) over the range of 300–600 nm. With the addition of excess NaClO, the absorption around 370–400 nm and fluorescence centered at 480 nm (**40a**, $\Phi = 0.036$) and 468 nm (**40b**, $\Phi = 0.047$) characteristic of the corresponding coumarin dyes, were observed as conjugation is extended. The probes, which featured high sensitivity, selectivity, fast response, and pH independency, were successfully utilized in detecting ClO[−] in aqueous media and living cells. Importantly, they were used to visualize the generation of endogenous ClO[−] in progranulocytes and macrophages.

Cyanine dyes have been widely used as NIR fluorescent probes.⁵⁷ Probe **41** was designed based on a Se-containing heptamethine cyanine dye, and functions as a rapid response, highly selective HOCl probe (Fig. 40). Because of the significant aggregation, **41** exhibits very weak fluorescence in phosphate buffer (20 mM, pH 7.4). Upon the addition of HOCl, the probe deaggregates and a strong fluorescent emission at 786 nm is observed. Probe **41** was used to detect HOCl in commercial fetal bovine serum, and to image HOCl in live mice.

Li and co-workers designed a novel two-photon turn-on probe **42** for HOCl based on 9-fluorenone covalently conjugated to two selenium-containing moieties (Fig. 41).⁵⁸ Reversible recognition ability of the probe was achieved through redox cycles at the Se center. Results showed reversible and instantaneous responses of the probe towards intracellular HOCl. Moreover, the probe was successfully applied to the two-photon imaging of HOCl levels in zebrafish and mice.

Very recently, Venkatesan and Wu, reasoning that organotellurium compounds are more electron rich than organosulfur and organoselenium compounds, developed a diphenyl telluride-functionalized BODIPY probe to image HOCl (Fig. 42).⁵⁹ Oxidation by HOCl affords in an increase in emission. Confocal fluorescence microscopy imaging using RAW264.7 cells showed that the probe **43** could be used to evaluate the role of HOCl in biological systems. The probe could be reduced back to the non-fluorescent reduced state upon addition of glutathione. Fluorescence produced by other ROS and RNS was negligible.

6. Oxidation of double bonds

In organic synthesis, olefinic C=C double bonds can undergo an oxidative cleavage reaction with HOCl under mild conditions. This results in various double bond cleavage products, including relatively unstable chlorinated species that can undergo further oxidation to more stable non-chlorinated species such as aldehydes and carboxylic acids. As shown in scheme 6, conjugation based on C=C bonds may be disrupted by HOCl to afford spectroscopic changes. Based on this concept, several probes have been developed for the detection of HOCl.

The Ma group designed and synthesized a ferrocene-based fluorescent probe **44**.⁶⁰ Due to an ICT process from the electron-donor ferrocene moiety to anthracene, **44** was non-fluorescent. Upon addition of HOCl, the cleavable double bond linked conjugated molecule was oxidized to produce 9-methylanthracene, 9-(chloromethyl)anthracene and 9,10-dione as confirmed by total ion chromatogram and GC-MS (Fig. 43). This induced 100-fold fluorescent emission enhancement at 441 nm (excitation at 360 nm) in phosphate buffer (30 mM, pH 7.4):THF 1:1 (v/v). Other species including Ag⁺, Al³⁺, Ca²⁺, Cd²⁺, Cu²⁺, Fe²⁺, Fe³⁺, Hg²⁺, Mg²⁺, Mn²⁺, Pb²⁺, Zn²⁺, Cl⁻, ClO₃⁻, ClO₄⁻, MnO₄⁻, NO₂⁻, NO₃⁻, H₂O₂, •NO, O₂^{•-}, •OH, and ROO• did not cause fluorescent enhancement. Moreover, **44** was cell membrane permeable, and could be used for fluorescence imaging of HOCl in HeLa cells.

Subsequently, a colorimetric and ratiometric fluorescent probe (**45**) consisting of a boron-dipyrromethene (BODIPY) dye conjugated with a 2-dicyanomethylene-3-cyano-2,5-dihydrofuran group was developed for the selective and sensitive detection of HOCl.⁶¹ The mechanism involves oxidative cleavage of the olefin linker between BODIPY and DCDHF (Fig. 44). The addition of HOCl to **45** triggered a decrease of the initial peak at 614 nm, and growth of new peak at 504 nm in PBS buffer (10 mM pH 7.4) containing 1% ethanol, 0.1% Triton X-100 (v/v). In an analogous manner, the fluorescent emission at 629 nm decreased, and the emission band at 520 nm increased. With properties such as colorimetric and fluorimetric dual-signaling and cell permeability, **45** showed great promise as an efficient tool for biological applications.

The Zhu team developed a water-soluble tricyanoethylene-derived colorimetric probe **46** for the fast and sensitive detection of ClO^- in phosphate buffer (20 mM, pH 7.4) (Fig. 45).⁶² Upon the addition of HOCl, the absorption band centered at 527 nm decreased sharply, accompanied by a solution color changed from pink to colorless. Probe **46** exhibited excellent selectivity toward ClO^- over other interfering species. Additionally, **46** could detect ClO^- quantitatively in the range of 0–120 μM with a detection limit of 4 μM .

Recently, a novel cyanine based near-infrared fluorescent and colorimetric dual-signal probe **47** was synthesized and characterized.² As shown in Fig. 46, the reaction mechanism, confirmed by mass spectra, is the electrophilic addition to the polymethine chain, followed by oxidative cleavage. The reaction of **47** with HOCl induced fluorescence quenching at 774 nm in phosphate buffer (50 mM, pH 7.4):EtOH 9:1 (v/v). Furthermore, the absorption peak at 710 nm of **47** decreased gradually as a new band at 520 nm grew, accompanied by a color change from blue to purple to pink (Fig. 46). With good cell membrane permeability and low cytotoxicity, **47** could be used as a new fluorescent probe for HOCl imaging in live cells. In addition, enzymatic activity of MPO could be evaluated on the basis of a colorimetric method.

7. Oxidation of cuprous to cupric

With strong coordination ability, Cu (II) is a widely used candidate for displacement detection of HOCl. Based on the reaction of HOCl that oxidizes Cu (I) to Cu (II) specifically, chemosensors that are unresponsive to Cu (I) but sensitive to Cu (II) have been developed for the indirect detection of HOCl (Scheme 7).

The Li group firstly applied a rhodamine derivative **48** for HOCl detection via copper oxidation (Fig. 47).⁶³ The UV-vis spectra of probe **48** with cuprous ions was nearly overlapped with the baseline in Tris buffer (10 mM, pH 7.0): CH_3CN 1:1 (v/v). Upon addition of HOCl, a new absorption peak at 555 nm appeared gradually, accompanied with a color change from colorless to magenta. Kinetics studies revealed that the detection process was complete within 6 min. Furthermore, representative species such as CO_3^{2-} , SO_4^{2-} , ClO_4^- , ClO_3^- , NO_2^- , AcO^- , and $\text{P}_2\text{O}_7^{4-}$ elicited no interference, except for H_2O_2 . With a detection limit as low as 0.81 μM , **48** could be used in real water samples.

Based on the previous work, another colorimetric ClO^- probe **49** was developed using an azobenzene acid by the Li team (Fig. 48).⁶⁴ Utilizing the oxidant of ClO^- properties of HOCl and the varying coordinating properties of Cu (I) and Cu (II), the addition of HOCl to the system of **49** and cuprous ions induced the red solution to turn yellow. Other anions, including HPO_4^{2-} , H_2PO_4^- , SO_4^{2-} , Cl^- , ClO_4^- , HSO_3^- , Br^- , PO_4^{3-} , CO_3^{2-} , I^- , HCO_3^- , SO_3^{2-} , F^- , AcO^- , HSO_4^- , NO_2^- , ClO_3^- , IO_3^- and H_2O_2 , has insignificant effect on the spectroscopic properties of **49** and ClO^- . The high sensitivity and selectivity of **49** can render it an efficient chemosensor for ClO^- in pure aqueous solutions.

The Yin group designed and synthesized a fluorescein derivative, **50**, for the detection of ClO^- (Fig. 49).⁷ Upon oxidation of Cu (I) to Cu (II), the colorless solution changed to magenta at pH 7.0. The Cu (II) complex was found to undergo further reaction to afford

green fluorescence upon storage for a few hours. Other common anions, including F^- , Cl^- , ClO_3^- , NO_2^- , CN^- , S^{2-} , SCN^- , $P_2O_7^{4-}$, AcO^- , CO_3^{2-} , SO_4^{2-} , ClO_4^- , did not interfere with ClO^- detection, except for H_2O_2 . The colorimetric and fluorescent responses made it promising for the detection of ClO^- in tap water.

In an interesting and somewhat related but unique recent study, Park *et al.* developed blue silver DNA-encapsulated nanodots that enable the effective detection of HOCl in industrial cleaners.⁶⁵

In addition, The Peng group developed a novel specific ratiometric nanoprobe **51** based on the FRET process (Fig. 50).⁶⁶ By embedding an aminocyanine dye as the ClO^- probe and the FRET acceptor, and rhodamine B as the FRET donor, the excitation wavelength at 550 nm would induce strong fluorescent emission at 750 nm. However, bleaching of aminocyanine dye by HOCl interrupted the FRET interaction, and the fluorescence spectrum of **51** exhibited a ratiometric change at 750 nm and at 575 nm. The large spectral separation eliminated the interference from each emission. A study of the reactivity of **51** towards various ROS, cations and anions confirmed its high selectivity towards ClO^- . The nanoprobe could further be used to visualize the ClO^- produced in HeLa cells.

The Chang group developed an HOCl-selective colorimetric and fluorogenic signaling probe **52** based on oxidation of a thiocarbonyl by HOCl (Fig. 51).⁶⁷ The absorption peaks of **52** at 325 nm and 443 nm decreased and a new band at 384 evolved upon the addition of HOCl to a solution of **52** in acetate buffer (10 mM, pH 4.8):CH₃CN 1:1 (v/v). The initially yellow solution turned colorless upon HOCl addition. HOCl was shown to induce a prominent (up to 250-fold) fluorescence enhancement at 465 nm. The detection limit of **52** towards HOCl was 0.83 μ M. Except for Hg^{2+} , in the presence of common metal ions and anions, probe **52** displayed high selectivity for HOCl. However, interference from Hg^{2+} ions was successfully removed by using Br^- as a masking agent. In chemical and environmental samples **52** could be useful for the determination of HOCl.

Concluding remarks

In this review, we have summarized recent progress towards the use of HOCl oxidation in the design of sensors and imaging agents for HOCl. The examples reported can be classified into seven reaction types according to their oxidation mechanisms. The oxidation of *p*-methoxyphenols, *p*-aminophenol analogues and oximes are the most widely used approaches for HOCl detection. Thioesters and amides mainly undergo chlorination reactions, whereas thioethers and selenides are generally oxidized to produce the corresponding sulfonate and selenoxide. The cleavage of carbon-carbon double bonds takes place in electron-rich conjugated probe systems. Probes exhibiting emission changes in the presence of HOCl are being and used in imaging and labeling. In addition, NIR dyes that are being modified to serve as HOCl probes will enable relatively deep tissue penetration and minimal auto-fluorescence background.^{2,4,5,30,51,57,66}

Importantly, probes that can evaluate the role of MPO, HOCl and other related species in biological processes promote vital progress and insight into human disease.^{2,4,30} For

example, the role of HOCl in regulating inflammation and cellular apoptosis is attracting increased current attention. As recently noted, however, the specific organelle(s) involved in the distribution of HOCl remain unknown.⁴⁷ Finally, effective tools for detecting HOCl at subcellular levels remains a major challenge due to its low concentration, strong oxidizing properties, and short lifetime. We hope that this review will inspire further research into the improved design of probes and sensors for HOCl that may help clarify its role in biology and enable its efficient environmental monitoring.

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Fig. 1.

The detection mechanism of probe **1** towards HOCl and structures of probe **2a**, **2b**, and **2c**.

Fig. 2.
The reaction of probe **3** and ClO^- .

Fig. 3.
The reaction of probe **4** and HOCl .

Fig. 4.
The reaction of probe **5** and HOCl.

Fig. 5.
The reaction of probe **6** and HOCl.

Fig. 6.
The reaction of probe **7** and HOCl.

Fig. 7.
The reaction of probe **8** and ClO^- .

Fig. 8.
The reaction of probes **9a** and **9b** with ClO⁻.

Fig. 9.
The reaction of probe **10** and ClO^- .

Fig. 10.
The reaction of probe **11** and ClO^- .

Fig. 11.
The reaction of probe **12** and ClO^- .

Fig. 12.
The reaction of probe **13** with HOCl.

Fig. 13.
The reaction of probe **14** and HOCl .

Fig. 14.
The reaction of probe **15** and HOCl.

Fig. 15.
The reaction of probe **16** and HOCl.

Fig. 16.
The reaction of probe **17** and ClO^- .

Fig. 17.
The reaction of probe **18** and HOCl.

Fig. 18.
The reaction of probe **19** and HOCl.

Fig. 19.
The reaction of probe **20** and HOCl.

Fig. 20.
The reaction of probe **21** and ClO^- .

Fig. 21.
The reaction of probe **22** and HOCl.

Fig. 22.
The reaction of probe **23** and ClO^- .

Fig. 23.
The reaction of probe **24** and HOCl.

Fig. 24.

Top: the reaction of probe **25** and HOCl . Bottom: proposed detection mechanism of HOCl .

Fig. 25.
The reaction of probe **26** and HOCl.

Fig. 26.
The reaction of probe **27** and ClO^- .

Fig. 27.
The reaction of probe **28** and HOCl.

Fig. 28.
The reaction of probe **29** and HOCl.

Fig. 29.
The reaction of probe **30** and HOCl.

Fig. 30.
Structures of the two-photon probes and the proposed detection mechanism.

Fig. 31.

Top: the reaction of probe **32** and ClO^- . Bottom: proposed detection mechanism.

Fig. 32.

Top: FRET-based ratiometric imaging of HOCl by probe **33**. Bottom: proposed oxidation mechanism.

Fig. 33.
Proposed detection mechanism of ClO^- detection using an AuNPs-dithiothreitol system.

Fig. 34.

Top: reaction of **35** with HOCl. Bottom: (A, C) absorption spectra and (B, D) emission spectra of **35** with HOCl in different pH buffer solutions (A, B, pH = 7.4). Reprinted with permission from *J. Am. Chem. Soc.*, **2013**, 135, 13365–13370. Copyright 2013, American Chemical Society.

Fig. 35.
The reaction of probe **36** and HOCl .

Fig. 36.
The reaction of probe **37** and HOCl.

Fig. 37.
The reaction of probe **38** and HOCl.

Fig. 38.
The reaction of probe **39** and HOCl.

Fig. 39.

Top: reaction of probe **40** and HOCl. Bottom: proposed detection mechanism of HOCl.

Fig. 40.
The reaction of probe **41** and NaClO.

Fig. 41.
The reaction of probe **42** and HOCl.

Fig. 42.
The reaction of probe **43** and HOCl.

Fig. 43.
The reaction of probe **44** and HOCl.

Fig. 44.
The reaction of probe **45** and HOCl/OCl⁻.

Fig. 45.
The reaction of probe **46** and ClO^- .

Fig. 46.

Top: reaction of probe **47** and HOCl. Bottom: (a) UV-vis responses of **47** to HOCl and the corresponding color changes. Reprinted with permission from *Anal. Chem.*, **2014**, 86, 671–677. Copyright 2014, American Chemical Society.

Fig. 47.
Proposed detection mechanism of ClO^- by probe **48**.

Fig. 48.
Proposed detection mechanism of HOCl by probe **49**.

Fig. 49.
Proposed detection mechanism of HOCl by probe **50**.

Fig. 50.
Proposed detection mechanism of HOCl when using probe **51**.

Fig. 51.
Reaction of probe **52** and HOCl.

Scheme 1.
The oxidation of *p*-methoxyphenol by HOCl.

Scheme 2.

The specific oxidation reaction between oximes and HOCl.

R = fluorophore

R' = SH, NH₂ or NH

Scheme 3.

The specific chlorination reaction between thiols or amides and HOCl.

Scheme 4.

The reaction of *p*-aminophenol analogues and HOCl.

R = fluorophore
R' = H or alkyl

Scheme 5.

The oxidation reaction between thioethers, selenides and HOCl.

Scheme 6.
HOCl-induced double bond cleavage.

Scheme 7.

The specific oxidation reaction of cuprous to cupric with HOCl.