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A fluoran-based fluorescent probe via a strategy of blocking the intramolecular photoinduced electron transfer (PET) process

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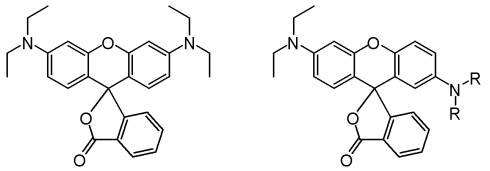
ABSTRACT

A novel fluoran-based fluorescent probe **2** has been designed and synthesized by using a strategy of blocking the intramolecular photoinduced electron transfer (PET) process. The probe keeps a ring-closed spirolactone structure in aqueous buffer solution. However, the oxidation of the probe by ClO^- perturbs a new equilibrium of the structural interconversion between the nonfluorescent spirolactone and the fluorescent ring-opened zwitterion, which generates a highly selective fluorescent probe for ClO^-. Meanwhile, the probe is cell membrane permeable and can be utilized as fluorescent probe for imaging ClO^- in living cells.

Reactive oxygen species (ROS) has attracted much attention in fluorescent probes for imaging in recent years because they mediate a variety of physiological and pathological processes.[1-3] Among ROS, HClO is a weak acid (pK_a = 7.6) and can partially dissociate to hypochlorite under physiological conditions, which is widely used in daily life as disinfectant, antimicrobial or bleaching agent with the concentration in the range of 10^{-5} - 10^{-2} M.[4] On the other hand, hypochlorous acid/hypochlorite ($HClO/ClO^-$) play important role in inflammation and the immune defense against microorganisms.[5] The endogenous ClO^- is biologically produced from peroxidation of Cl^- ions catalyzed by the enzyme myeloperoxidase (MPO) mainly in leukocytes,[6] including neutrophils, macrophages and monocytes.[7] However, maintaining a reasonable ClO^- concentration within the physiological environments is crucial for numerous cellular functions. Excessive or uncontrolled production of ClO^- can cause tissue damage and diseases, including arthritis,[8] cancers,[9] and neurodegeneration.[10] Therefore, simple, sensitive and reliable method for detection of ClO^- is urgently needed.

Fluorescent probes have been widely developed for ClO^- detection in the past decade due to their high sensitivity, high selectivity and real-time detection.[11,12] In recent years, a great variety of fluorophores were employed in the design of chemosensors for ClO^-, such as rhodamine, fluorescein, 1,8-naphthalimide, cyanine, coumarin, phenothiazine, etc.[13] Among them, a general strategy for the design of fluorescent probes for ClO^- is to connect an organic fluorophore with an easily oxidized moiety by taking advantage of the strong oxidation property of ClO^-, which produce optical signal changes corresponding to the process of oxidation. It is well known that fluoran dyes, another type of dyes containing xanthene chromophore,[14] were widely used as thermosensitive dyes in print industry by taking full advantage of the thermo-controlled ring-opening process of the spirolactone (Scheme 1).[15] However, only a small amount of fluoran-based chromogenic chemosensors were developed for sensing of ions.[16-18] To the best of our knowledge, no fluoran-based fluorescent probe has been reported up to date.



Scheme 1 Structures of rhodamine and fluoran dyes.

During the investigation of the optical properties of the known fluoran dye **1**[19] (Scheme 2), we found that the dye exhibited a stable ring-opened zwitterionic structure as shown in Fig 1a in water phase from pH 5 to 10, and with its characteristic π-π* transitions absorption band at ca. 550 nm. While the pH value is lower than 4, the maximum absorption band of **1** was blue shifted to ca. 455 nm due to the protonation of the amino group (Fig. S1a). However, the fluoran dye **1** only showed strong fluorescence with the pH value lower than 4 (Fig. S1b). The results can be rationalized that even though the fluoran dye **1** keeps a ring-opended zwitterionic structure from pH 5 to 10, its fluorescence signal is quenched by the free amino group via a

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PET mechanism from the electron-donating N atom to the excited state of the fluorophore, resulting in the fluorescence signal quenching (Fig. 1b).

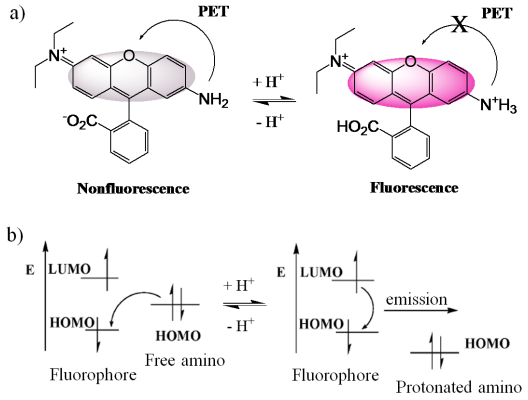
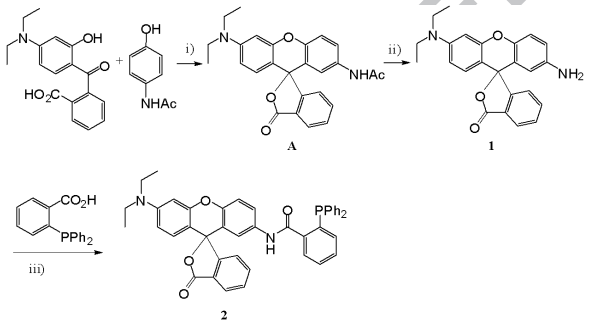


Fig. 1 a) Proposed fluorescence emission mechanism of fluoran **1**. b) the PET mechanism of **1**.

Inspired by the aforementioned optical properties of the fluoran dye **1**, we hypothesized that the introduction of electron-deficient functional group on the amino group may decrease its energy level of the highest occupied molecular orbital (HOMO), and prevents its electron transfer to the excited state of the fluorophore, resulting the fluorescence recovery of the fluorophore. Based on this hypothesis, we reported herein a novel fluoran-based ClO^--selective fluorescent probe **2** by introducing an electron-deficient diphenylphosphinobenzoyl group on the amino group to decrease its HOMO level. It is also important to note that a few of P(III) atom containing probes have been reported for H_2O_2 or other ROS detections by using the P(III)/P(V)-involved PET on/off control.[20] Probe **2** exhibits a high sensitivity and high selectivity for ClO^- detection. Meanwhile, the probe is cell-permeable and can be used for imaging ClO^- in the living cell.



Scheme 2 Synthesis of the probe **2**, reagents and conditions: i) 98% H_2SO_4, 55 °C, 24 h; ii) ca. 36% H_2SO_4, 95 °C, 4 h; iii) DIEA, HATU, dry CH_2Cl_2, 12h, Ar.

The synthetic route for probe **2** was shown in Scheme 2. To synthesize the probe **2**, compound **1** was prepared according to the literature[20] by condensation of 4-acetylamino-phenol with 2-(4-(*N*,*N*-diethylamino)-2-hydroxyben-zoyl)benzoic acid via a conveniently acid-promoted Friedel-Crafts acylation protocol in concentrated H_2SO_4, and subsequently was hydrolyzed in dilute H_2SO_4 to remove the acetyl group. Finally, probe **2** was obtained in 35% yield through the reaction of compound **1** with 2-(diphenylphosphino)benzoic acid in the presence of condensation agent 2-(7-aza-1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HATU) in anhydrous dichloromethane (Scheme 2) under Ar atmosphere. The structure of **2** was characterized by high-resolution mass spectrometry (HRMS), ^{1}H- and ^{13}C-NMR spectra analyses (see supporting information).

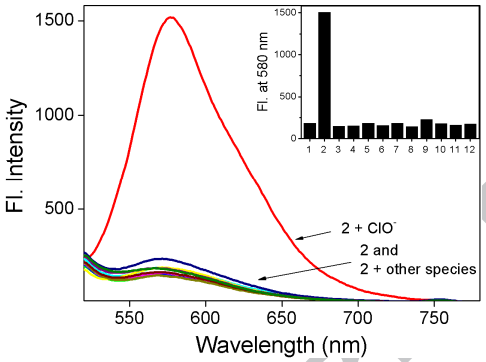


Fig. 2 Fluorescence emission changes of probe **2** (5 μM) upon addition of various ROS (30 μM) in PBS buffer (10 mM, EtOH /H_2O = 1/4, pH 7.4). Inset: fluorescence intensity changes at 580 nm. 1-12: probe, ClO^-, H_2O_2, TBHP, $^{\cdot}OH$, $ONOO^-$, $O_2^{\cdot-}$, NO, $^1O_2$, NO_2^-, NO_3^- and AS; λ_{ex}: 500 nm, Slit: 10 nm, 10 nm.

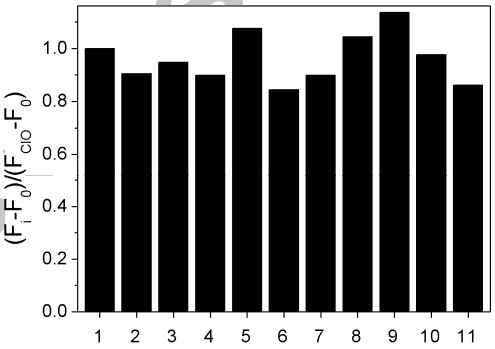


Fig. 3 Fluorescence intensity changes [$(F_i-F_{Probe})/(F_{ClO^-}-F_{probe})$] of probe **2** (5 μM) at 580 nm towards ClO^- (6 equiv.) in the presence of other ROS(6 equiv.) in PBS buffer (0.01 M, EtOH/H_2O = 1/4, pH 7.4). 1 - 11: ClO^-, H_2O_2, TBHP, $^{\cdot}OH$, $ONOO^-$, $O_2^{\cdot-}$, NO, $^1O_2$, NO_2^-, NO_3^- and AS; λ_{ex}: 500 nm, Slit: 10 nm, 10 nm.

Firstly, the absorption and fluorescence responses of the probe **2** in the absence and the presence of various ROS were performed in PBS buffer (10 mM, EtOH/H_2O = 4/1, pH 7.4). As shown in Fig. S2, probe **2** (5 μM) exhibited weak absorption band over 400 nm, indicated that the probe keeps a ring-closed spirolactone structure in aqueous buffered solution. Nevertheless, the addition of ClO^- induced two significant absorption peaks at ca. 500 nm ($\varepsilon = 1.72 \times 10^4$ M^{-1} cm^{-1}) and 535 nm ($\varepsilon = 1.52 \times 10^4$ M^{-1} cm^{-1}), respectively, accompanied by significant color change from nearly colorless to faint red, which may correspond to the ClO^--elicited ring-opened form of the probe. In contrast, the addition of other ROS contributed to no significant absorption or color changes (Fig. S3). When excited at 500 nm, the probe (5 μM) exhibited weak fluorescence at around 580 nm under the same conditions (Fig. 2). Among the ROS tested, the probe only showed significant fluorescence enhancements at 580 nm with ClO^-, the addition of other ROS induced no obvious fluorescence changes of the probe. It is noted that diphenylphosphinobenzoate moiety was commonly used as a candidate for HNO recognition.[21, 22] However, we found Angeli's salt (AS, as a HNO processor) elicited no obvious fluorescence changes compared with the fluorescence spectra of the probe alone. Subsequently, the competition experiments were carried out to evaluate fluorescence changes of the probe towards ClO^- in presence of other ROS. As can be seen from Fig. 3, the fluorescence response of the probe towards ClO^- is not influenced by the presence of

other ROS. The results clearly suggested the probe can respond to ClO^- with high selectivity among various ROS.

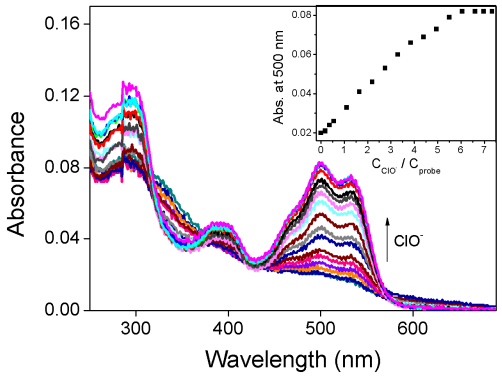


Fig. 4 Absorption titration spectra of probe **2** (5 μM) in PBS buffer (0.01 M, EtOH/H_2O = 1/4, pH 7.4) upon addition of ClO^- (0 - 36.6 μM). Inset: the plot of absorbance intensity as a function of the concentration ratio of C_{ClO^-}/C_{Probe}.

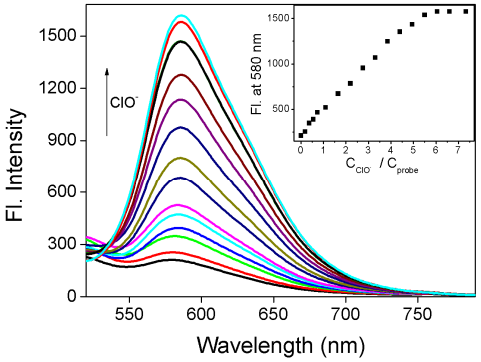
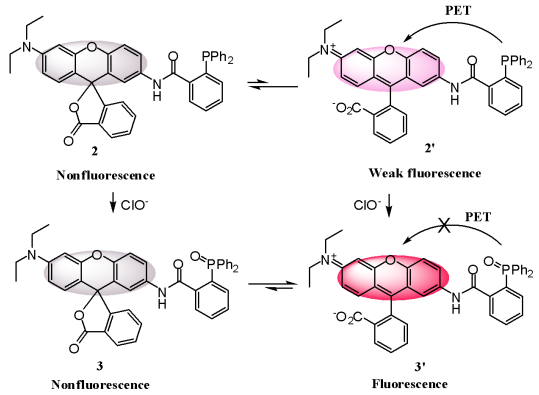


Fig. 5 Fluorescence titration spectra of probe **2** (5 μM) in PBS buffer (0.01 M, EtOH/H_2O = 1/4, pH 7.4) upon addition of ClO^- (0 - 36.6 μM). Inset: the plot of fluorescence intensity as a function of the concentration ratio of C_{ClO^-}/C_{probe}. λ_{ex}: 500 nm, Slit: 10 nm, 10 nm.

To apply the probe in more complicated systems, pH-dependence experiments were investigated in the presence and absence of ClO^- by absorption and fluorescence spectra. The absorption changes of probe and probe/ClO^- systems under different pH values were illustrated in Fig. S5. From pH 4 to pH 10, no significant absorption changes were observed for the probe. In contrast, in the presence of ClO^-, the probe exhibited an obvious absorption enhancement at 500 nm from pH 4 to 10. The absorption intensity reached a maximum at pH 4.0 and had a gradual decrease in pH range 4 - 7, and then no obvious changes can be observed from pH 7 to 10. The pH profile evaluated by fluorescence spectra also exhibited the same tendencies as determined by absorption spectra (Fig. S6). The results indicated that **2** can be utilized as ClO^--selective probe over a broad pH range (pH 4 - 10). Finally, the time-dependent fluorescence responses of **2** under excitation at 500 nm were evaluated in the absence and presence of ClO^-. As shown in Fig. S7, a weak fluorescence signal was observed with the free probe in PBS buffer (10 mM, EtOH/H_2O = 1/4, pH 7.4). However, the fluorescence intensity increased immediately at the first 120 seconds and reached its maximum within 5 min after the addition of ClO^- (6.0 equiv.), indicated that the reaction event between the probe **2** and ClO^- could complete in less than 5 min. Based on the aforementioned absorption and fluorescence changes before and after the addition of ClO^-, we suggested the spectra changes of the probe **2** are relevant to the oxidation of P atom by ClO^- and subsequent ring-opened cascade reaction processes. As shown in scheme 3, the probe in aqueous buffered solution exhibits mainly in the form of spirolactone **2** and a very minor portion of ring-opened zwitterionic structure **2'**, which correspond to a very weak absorption at ca. 500 nm and a weak fluorescence emission at 580 nm. Along with the oxidation of P atom by ClO^-, the probe **2** was converted to spirolactone **3**. However, the oxidation of **2** perturbs a new equilibrium of the structural interconversion between the spirolactone **3** and the ring-opened zwitterion **3'**. The absorption and fluorescence spectra indicated that the oxidized product **3** exhibits mainly in the form of ring-opened zwitterion **3'** (Fig. 4 and Fig. 5). On the other hand, the electron-rich P atom within the probe **2** can partially quench the fluorescence of the ring-opened zwitterionic structure **2'** via PET process (Scheme 3), which was further proved by absorption and fluorescence spectra (Fig. S8). Upon the addition of trifluoric acetic acid (TFA), the absorption and fluorescene intensities of **2** are obviously increased. However, the addition of ClO^- to the acidic solution of **2** induced no more increase of the absorption intensity (Fig. S8a), nevertheless, along with the oxidation of the P atom by ClO^- it elicited an obvious fluorescence enhancement which suggested the block of the PET process from the electron-donating P atom to the excited state of the xanthene fluorophore (Fig. S8b). To get more solid evidence that the recognition process is the oxidation of P atoms by ClO^-, the reaction mixture of the probe **2** with ClO^- was further investigated by the high resolution mass spectra (HRMS). As shown in Fig. S9, the most abundant peak at m/z $[M + H]^+$ = 691.2389 and a weak peak at m/z $[M + Na]^+$ = 713.2207 corresponding to $[\mathbf{3'} + H]^+$ [calc. m/z 691.2362] and $[\mathbf{3'} + Na]^+$ [calc. m/z 713.2181], respectively, demonstrated the oxidation of P atom by ClO^-. To further elucidate the structure of product **3** and/or **3'**, the reaction between **2** and ClO^- was investigated. After purified by column chromatography. It was obtained as yellowish-brown solid in 41% yield. It showed a typical P(V) ^{31}P NMR spectrum at 35.452 ppm (Fig. S10). Compared with **2** (δ = -10.268 ppm), it is largely downfield-shifted (over 45 ppm). Due to the structure conversion between **3** and **3'**, its ^1H and ^{13}C NMR are difficult to assignments (Fig. S11 - S12).



Shcheme 3 Proposed structural interconversions of the probe **2** before and after the addition of ClO^-, and their fluorescence properties.

To further evaluate practical applicability of **2**, it was employed in fluorescence microscopy images of living L929 cells. The cultured L929 cells were incubated with the probe **2** (3 μM) in culture medium at 37 °C for 1 h, and then washed with PBS buffer to remove excess probes. As shown in Fig. 6, laser scanning confocal microscopy image showed that the L929 cells treated with the probe for 1 h gave very weak intracellular fluorescence signals (Fig. 6b). Upon treatment with 3 equivalents of ClO^- under the same conditions, the cells pretreated with the probe exhibited significant fluorescence enhancement in intensity (Fig. 6d). These results demonstrated the probe is cell membrane permeable and can be used for imaging ClO^- in living cells.

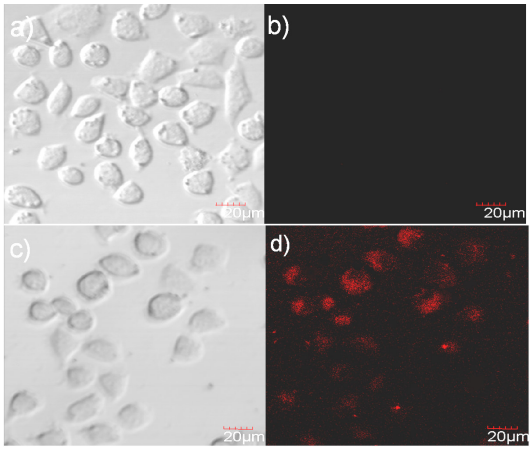


Fig. 6 Confocal fluorescence images of living L929 cells. (a - b) Cells was incubated with **2** (3 μM) for 1 h; (c - d) the cells loaded with **2** (3 μM) for 1 h; then treated with ClO^- (9 μM) for 30 min. (a) and (c): bright field image; (b) and (d): red channel at 574 - 638 nm. λ_{ex}: 488 nm, Scar bars: 20 μm.

In summary, the first fluoran-based fluorescent probe **2** has been designed and synthesized by using a strategy of blocking the intramolecular PET process. The probe keeps a nonfluorescent ring-closed spirolactone structure in aqueous buffer solution. However, the oxidation of the P atom within probe by ClO^- induces a conversion from the nonfluorescent spirolactone to the fluorescent ring-opened zwitterion, which generates a high selective fluorescent probe for ClO^-. Meanwhile, the probe exhibits cell membrane permeability and can be used for imaging ClO^- in the living cell.

Acknowledgments

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Supplementary Material

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org.

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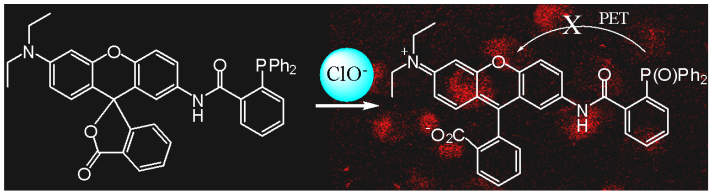

Highlights

>A fluoran-based fluorescent probe has been prepared.

>The probe exhibits high selectivity and sensitivity towards ClO^-.

>The probe can be used for imaging of ClO^- in living cells.