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Single probe giving different signals towards reactive oxygen species and nitroxyl

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A B S T R A C T

The first multi-channel probe giving different signals towards ROS and nitroxyl has been easily synthesized with a rational method which successfully showed blue emission towards peroxynitrite and hypochlorite and green emission towards nitroxyl in solution. The highly efficient oxidation of hypochlorite towards triphenylphosphine was discovered and utilized to distinguish hypochlorite and peroxynitrite with the aid of nitroxyl. A rare photoinduced electron transfer (PET) phenomenon from the donor fluorophore to the acceptor fluorophore was observed and adopted to give the signal of sequence sensing. Furthermore, the probe gave real-time signal selectively towards peroxynitrite and nitroxyl in Hela cells.

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Reactive oxygen species (ROS) is a collective term, which includes radicals such as hydroxyl radical (·OH), superoxide anion radical ($O_2^{\cdot-}$) and certain non-radical oxidants such as hydrogen peroxide (H_2O_2), singlet oxygen (O_2^1) and hypochlorous acid (HOCl). Low concentrations of ROS are beneficial for defence against microbial infection but become harmful when the balance between their production and removal/inactivation by antioxidant defence system is weakened [1]. Another important reactive species are reactive nitrogen species which include nitric oxide (NO), peroxynitrite ($ONOO^-$) and nitroxyl (HNO). $ONOO^-$ is generated through the reaction of nitric oxide and superoxide anion radicals under diffusion control without the need of enzymatic catalysis which can also be seen as a member of ROS [2]. Peroxynitrite and HOCl are highly reactive oxygen species (hROS). Hypochlorous acid easily undergoes chlorination reactions (cholesterol and DNA) as well as oxidation reactions (glutathione and proteins) which may lead to diseases such as atherosclerosis [3]. Overproduction in peroxynitrite leads to oxidation of mitochondrial and cell proteins, lipids, DNA with resulting adverse effects such as apoptosis [4]. HNO, the one-electron-reduced form of NO, remains to be an enigmatic reactive nitrogen species which has been broadly used as treatments for heart failure [5]. Besides the readily reaction with biothiols, it can also react with oxygen to produce $ONOO^-$ [6]. HNO can be endogenous generated through the following possible ways: the reduction of NO by superoxide dismutase [7,8] or cytochrome *c* [9] and the reduction of S-nitrosothiols by low molecular weight protein thiols [10,11]. Recent literature also report that HNO can be endogenous produced from the oxidation of hydroxylamine, hydroxyurea, and acetohydroxamic acid by HClO [12]. As a matter of fact, whether these relevant reactive species act synergistically in physiological and pathological process and the specific correlation between them haven't been widely discussed and thoroughly understood which makes it meaningful to develop tools to track them.

Fluorescent probes are very effective and convenient tools to monitor these short-lived and reactive species due to simple manipulation, high sensitivity, and real-time in situ observation [13]. However, using different probes together may cause problems like different localization and interference. Herein, we demonstrate a facile constructed probe giving different signals towards ROS ($ONOO^-$ and HClO) and nitroxyl in solution shown Scheme. 1a. What's more, the probe successfully gave real-time signal selectively towards peroxynitrite and nitroxyl in Hela cells. The main working mechanism was illustrated in Scheme. 1b. The most widely used boron ester was chosen as the ROS trapper and triphenyl phosphine was chosen as the nitroxyl trapper to undergo the Staudinger reaction [14]. The synthetic procedure was direct and simple without laborious work in separation shown in Schemes

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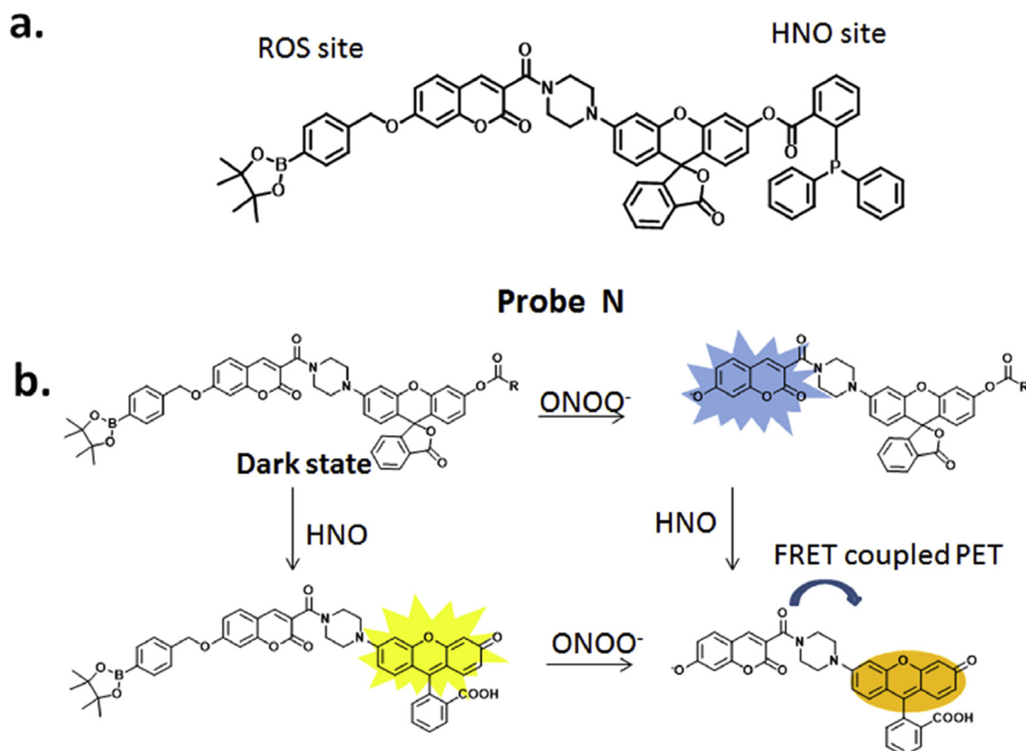

Scheme 1. Structure of Probe N and its working mechanism.

S1–S2. In order to circumvent the partial hydrolysis of the boron ester when the carboxyl ester of the coumarin was hydrolysed in the conventional way, a rational and novel method was adopted shown in Scheme S1.

First of all, we tested the reactivity of Probe N towards different ROS. $ONOO^-$ was found to react with Probe N very fast and only a few equivalent of $ONOO^-$ was needed to consume the boronate under the condition of acetonitrile/PBS (20 mmol) 5:5. As shown in Fig. S1, the reaction of 10 μM probe N with 40 μM $ONOO^-$ could be finished within 3 min, and the intensity of the blue emission was 200 times stronger than the sample without $ONOO^-$ (Fig. 1a). The fluorescence at 452 nm of 7-hydroxyl-coumarin excited with 405 nm increased in an almost linear way ($R^2 = 0.98$) in the range of 0–50 μM $ONOO^-$. From the absorption spectra in Fig. S2, only a little increase at 510 nm belonging to the ring-opening rhodol moiety appeared which might be caused by excessive sodium hydroxide as stabilizer in $ONOO^-$ stock solution induced hydrolysis of the phenol ester. However, no obvious fluorescence at 540 nm of the ring-opening rhodol moiety could be observed when 80 μM $ONOO^-$ was added shown in Fig. 2 that suggested the detection of $ONOO^-$ wouldn't cause interference or false signal of HNO. Next, the reaction towards hypochlorite was tested. Seen from Fig. S3, the reaction with 40 μM hypochlorite could be finished within 20 min which was much slower than $ONOO^-$. Like the reaction with $ONOO^-$, with the addition of hypochlorite, peaks in absorption spectra (Fig. S4) at 400 nm which attributed to the hydroxyl coumarin increased steadily and no peaks at 510 nm could be observed which means no interference existed. Meanwhile, the fluorescence at 456 nm excited with 405 nm light increased as expected with relative good linearity ($R^2 = 0.994$ in the range of 10–40 μM) as it is shown in Fig. 1b. Considering the slopes of the standard working curve of the probe towards both $ONOO^-$ and NaClO were almost in the same region, Probe N could give a global quantity of $ONOO^-$ and NaClO in solution. Interestingly, the mass spectrum showed that Probe N was transformed into the 7-hydroxyl-coumarin form with the triphenylphosphine oxidized into the phosphine oxide by 100 μM NaClO efficiently as shown in Fig. S13 [15], while obvious MS peak of the 7-hydroxyl-coumarin with the triphenylphosphine recognition group could still be found with 100 μM $ONOO^-$ as shown in Fig. S15. Then 300 μM hydrogen peroxide was added, and about 50 min were needed for the fluorescence to reach to the intensity where 40 μM $ONOO^-$ or NaClO was added (Fig. S5). That is to say, Probe N was more suitable for real-time imaging small amount of peroxynitrite or hypochlorite with the boronate group in solution, and the same conclusion and brief understanding about this result were reported in the literature [16].

Then whether the platform could sense HNO was tested. As shown in Fig. 1c, after incubating Probe N with different concentration of Angeli's salt (donor of HNO) for 30 min, the fluorescence at 540 nm belonging to the ring-opening rhodol form increased dramatically ($R^2 = 0.96$ in the linear range (5–30 μM), and about 40 μM HNO was needed to saturate the emission. The reaction with 40 μM HNO only required 10 min to finish (Fig. S7). Seen from the absorption spectra in Fig. S6, about 60 μM HNO was needed to complete the reaction. Unlike the spectra in Figs. S2 and S4 where the absorption between 300 and 450 nm were mutually transformed, the steady increase of the absorption between 380 and 420 nm after deprotection of the phenol on rhodol might be caused by the spatial interaction or adjacency of the benzyl alkoxyl coumarin moiety and the ring-opening rhodol moiety. And because of the existence of the absorption, emission at 540 nm could actually reach to a moderate intensity excited with 405 nm (Fig. S11), which means the platform is not suitable for the dual-site reacted FRET turn-on working mode in solution cause false signal might be caused. The results demonstrated that Probe N was capable of giving different signals towards ROS and nitroxyl in solution separately. The selectivity of Probe N towards other ROS/RSS/RNS was also tested. As it is shown in Fig. 2, besides a little

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