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A highly sensitive fluorescent probe for ozone based on coumarin-benzothiazole derivative

Kangni Chen[1], Yanbo Li[2], Jinyan Shang[1], Chao Zhao[1] and Heping Li[1*]

Abstract

Ozone is widely used in daily life, but studies have shown that O_3 can damage human trachea and lungs, leading to diseases such as asthma, emphysema, and bronchitis. Therefore, it is of great significance to develop a simple and efficient detection method for monitoring O_3 in living cells. In this study, 3-(but-3-en-1-yl)-2-(7-(but-3-en-1-yloxy)-2-oxo-2H-chromen-3-yl)benzo[d]thiazol-3-ium (BCT) as a new type of water-soluble fluorescent probe was synthesized by substitution reaction of 4-bromo-1-butene and hydroxycoumarin-benzothiazole derivatives, which can specifically detect ozone in aqueous solution. The interaction of ozone on the probe can be completed within 20 min, the fluorescence intensity is significantly enhanced, and it has the advantages of high sensitivity (detection limit LOD = 43 nM). The influence of pH on the fluorescent performance of BCT shows that the probe with super stability under weak alkali and acidic environment, which provides the necessary conditions for its detection of ozone in physiological system detection. Therefore, BCT is expected to become an effective tool for detecting ozone in cellular organisms.

Keywords: Ozone, Fluorescent detection, Coumarin-benzothiazole fluorescent probe, Photo-induced electron transfer (PET)

Introduction

As a strong oxidant, ozone (O_3) is widely used in the fields of water purification, air treatment, food preservation, deodorization, and medical treatment (Oyama 2000; Boeniger 1995; Baysan and Lynch 2005). However, there is evidence that high concentrations of O_3 can damage human trachea and lungs, leading to diseases such as asthma, emphysema, and bronchitis (Kim et al. 2011; Yan et al. 2013). In 2002, Wentworth reported the ozone produced by singlet oxygen in the inflammatory response of atherosclerotic plaque and neutrophils (Wentworth Jr et al. 2002; Wentworth Jr. et al. 2003). Since then, O_3 has been widely studied as an oxidant harmful to human health, but there is still a lack of detection methods suitable for monitoring O_3 in living cells, which is not conducive to further research on the mechanism of O_3 harming human health.

The current methods of detecting O_3 mainly include electrochemiluminescence, bioluminescence, and chemiluminescence. For example, Takeuchi developed a chemiluminescence method using indigo-5, 5-disulfonate (IDS) to identify ozone (Takeuchi and Ibusuki 1989), but it can also identify superoxide (Kettle et al. 2004). Ishii used boron-doped diamond (BDD) electrodes for electrochemical detection of ozone dissolved in water (Ishii et al. 2013). However, due to the extremely strong oxidation characteristics of ozone, the materials that can be used for sensing electrode are limited to a few precious metals and diamonds, which are expensive electrode materials. Koide's group used the mechanism of terminal olefins to specifically recognize

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ozone for the first time and designed small organic molecule probes that specifically responded to ozone (Garner et al. 2009; Leslie et al. 2011; Li et al. 2013). Compared with other detection methods, the fluorescence method has the best effect on detecting ozone. It can overcome the interference of other superoxides, thereby improve the accuracy of detection. O_3 has a lower concentration and a shorter life span in living cells. Therefore, it is of great significance to develop a simple and efficient organic small molecule fluorescent probe for monitoring O_3 in living cells. Among various fluorescent dyes, coumarin derivatives are widely used in the construction of selective fluorescent probes because of their advantages such as high molar extinction coefficient, high fluorescence quantum yield, and optical stability (Liao et al. 2016). Benzothiazole compounds also have good fluorescence properties due to their large conjugated system (Sun et al. 2012). Therefore, based on the coumarin-benzothiazole derivatives, combined with the mechanism of terminal olefin specific recognition of ozone, a new type of organic small molecule fluorescent probe 3-(but-3-en-1-yl)-2-(7-(but-3-en-1-yloxy)-2-oxo-2H-chromen-3-yl)benzo[d]thiazol-3-ium (BCT) was constructed. Synthetic method of BCT is simple, the raw materials are readily available, and the purification treatment adopts a simple and efficient recrystallization method, which avoids heavy and inefficient column chromatography purification. The probe can quickly identify ozone and has specific selectivity to ozone, so the probe has broad application prospects in ozone detection.

Materials

The water used in the experiment was deionized. The raw materials and other reagents used for the synthesis of probes in the experiment were of analytical grade. Purchase the corresponding chemical reagents from Maclean or Aladdin. The ozone used for the detection was prepared on-site from an electrolytic ozone generator purchased from Wuhan Weimeng Environmental Protection Technology Co., Ltd, and immediately tested on-site. The ozone-dissolving solution was 10 mM PBS buffer, and its concentration was determined by ultraviolet absorption spectrum (λmax=258 nm; εO_3= 2900 L mol^{-1} cm^{-1}) (Fan et al. 2013) and iodometric titration. Other reactive oxygen species (ROS) used in selective experiments were prepared as follows: hydrogen peroxide (H_2O_2), sodium hypochlorite (NaClO), and tert-butyl hydroperoxide (TBHP) are solutions of 30%, 10%, and 70%, respectively; Superoxide anion radical (O_2•−) was prepared from potassium peroxide (KO_2) and dimethyl sulfoxide (DMSO); Singlet oxygen ($^1O_2$) was prepared from NaClO and H_2O_2 with a mass ratio of 1:1; The hydroxyl radical (•OH) was prepared from Fe(II)EDTA; H2O2 with a mass ratio of 1:6; Prepare a 5 mM probe stock solution by dissolving the probe in dimethyl sulfoxide (DMSO). Unless otherwise stated, the buffer solution used in the experiment was a 10 mM PBS buffer solution.

Instrumentation

An ultraviolet-visible spectrophotometer (Shimadzu, Japan) was used to measure the ultraviolet absorption spectrum (UV-vis). The fluorescence emission spectrum was recorded using an F-7000 fluorescence spectrophotometer (Hitachi, Japan). Using TMS as an internal reference, ^1H NMR spectra were recorded on a Varian INOVA-400 nuclear magnetic resonance spectrometer High-resolution mass spectrum (HRMS) was performed on the LTQ Orbitrap XL massspectrometer. The pH value was measured using a Mettler-Toledo Delta320 pH meter. Other instruments include an upright rotary evaporator, SHB-III type water circulation multi-purpose vacuum pump, and X-5 micro-melting point measuring instrument.

Sample preparation

Took 4990 μL of PBS buffer (pH=7.4) and 10 μL of the prepared 5 mM probe stock solution into a 10 mL ep tube, added a freshly prepared O_3 aqueous solution and mixed. The excitation wavelength of the fluorescence spectrum test was 425 nm, the excitation slit was 5 nm, the emission slit was 5 nm, and the photomultiplier tube voltage was 700 V. All data were measured in parallel three times.

Test of the effect of O_3 concentration on the fluorescence of probe molecules: 10 μL probe BCT stock solution was added to 10 groups of 10 mL ep tubes, diluted to 5 mL with PBS buffer, and then 20 μL O_3 aqueous solutions of different concentrations (0, 1, 4, 8, 12, 15, 17, 20, 23, 25 μM). After 10 min of incubation at room temperature, the UV-vis and fluorescence spectra were tested.

Selective testing of BCT probes for cations, different reactive oxygen species and amino acids: 17 groups of 10 μL probe BCT stock solutions were transferred to 10 mL ep tubes, diluted to 5 mL with PBS buffer, and 0.4 mL of various cation aqueous solutions were added to the mixture, and the resulting mixture was shaken. Then let it stand for 10 min, and scan each solution with a fluorescence spectrophotometer to obtain its fluorescence properties.

Test of the influence of pH on the fluorescence spectrum of BCT: 10 μL probe BCT stock solution was added to ep tubes, diluted to 5 mL with PBS buffer, and the pH value of each solution was adjusted with dilute HCl and dilute NaOH aqueous solution to make 10 groups pH 6-8, respectively. Then add 10 μL of probe

BCT stock solution to ep tubes, dilute to 5 mL with PBS buffer, then add the same amount of O_3 aqueous solution with the same concentration, and adjust each ep with dilute NaOH and dilute HCl aqueous solution to make 10 groups pH 6-8, respectively. Shake these ep tubes well and let them stand for 10 min at room temperature, and then test the fluorescence spectrum properties of the 20 groups of solutions.

Response time test of the action of BCT and O_3: 10 μL of probe BCT stock solution was added to a 10 mL ep tube, diluted it to 5 mL with PBS buffer, and then added 0.4 mL O_3 solution to it. The solution was immediately transferred to a fluorescent colorimeter, used a fluorescence spectrophotometer to scan the fluorescence intensity over time.

Synthesis of probe BCT

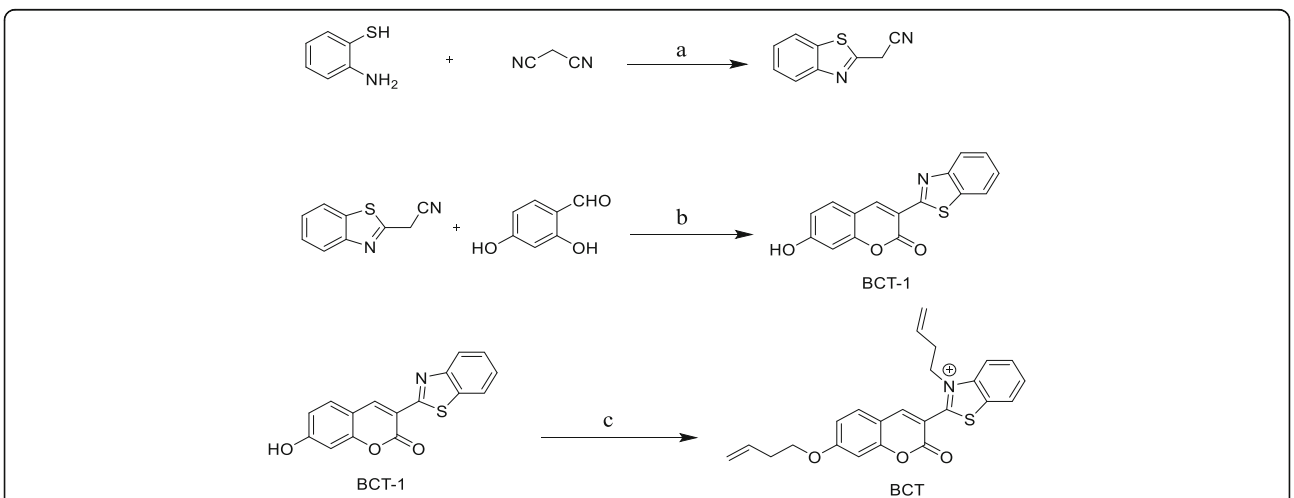
As shown in Scheme 1, dissolve BCT-1 (295 mg, 1 mmol), K_2CO_3 (120 mg, 0.91 mmol) and 4-bromo-1-butene (86.4 uL, 0.86 - 2 mmol) in 5 mL DMF, stir the mixture and heat to 70 °C, After the reaction proceeded for 24 hours, the mixture was poured into water (25 mL), and extracted with EtOAc (40 mL× 3). The combined organic layer was washed with water and brine, dried over anhydrous Na2SO4, filtered and concentrated in vacuo, and the crude product was purified by recrystallization using EtOAc to obtain 0.255 g of a yellow solid product with a yield of 73%. The ^{1}H NMR and ^{13}C NMR spectra and HRMS of BCT are given in Figures S2 and S3, respectively. ^{1}H NMR(400 MHz, CDCl3): δ 8.53(s,1H), 8.40 (d, J = 8.9 Hz,1H), 8.08–8.04 (m,1H), 7.85 (d, J = 8.0 Hz,1H), 7.49 (d, J = 7.2 Hz,1H), 7.38 (t, J = 8.1 Hz, 1H), 6.60 (dd, J = 8.9, 2.3 Hz,1H), 6.45 (d, J = 2.3 Hz,1H), 5.96–5.85 (m,2H), 5.29–5.12 (m,4H), 4.12–4.07 (m,4H), 2.67–2.62 (m,2H), 2.58–2.54 (m,2H). ^{13}C NMR (101 MHz, CDCl3): δ 164.33, 160.01, 153.82, 141.70, 134.62, 134.00, 130.42, 126.69, 125.68, 123.56, 121.49, 118.24, 115.11, 106.55, 102.12, 99.62, 67.80, 33.58. HRMS (ESI Positive) calc. for $C_{24}H_{22}NO_3S^+$, $[M+H]^+$ 350.0849. found 350.0806 (Figure S1).

Results and discussion

Based on the characteristics of coumarin and benzothiazole dyes (Wang et al. 2015; Fang et al. 2019), the benzothiazole heterocycle was introduced into the 3 positions of the coumarin ring. The purpose of this design is to improve the properties of the fluorophore. The conjugation of coumarin and the benzothiazole ring leads to an increase in the conjugate system and an increase in the Stokes shift. The fluorescence emission wavelength of the probe BCT is at 550 nm, which is 100 nm red-shifted compared to the common coumarin emission wavelength and emits bright green fluorescence. The introduction of 4-bromo-1-butene as the recognition group at position 7 realizes the specific recognition of ozone. The synthetic route is shown in Scheme 1. The structure of the probe BCT was characterized by HRMS (Figure S1) and NMR (Figure S2, S3).

Study on spectral performance of BCT

Ultraviolet absorption experiments were performed using aqueous solutions containing different concentrations of O_3 in a PBS solution with a probe concentration of 10 μM (PBS buffer: 10 mM, pH=7.4). It can be seen from Fig. 1 that the probe BCT has a strong absorption peak at 425 nm. As the ozone concentration increases, the absorbance at 425 nm gradually decreases, and the maximum absorption wavelength does not blue shift, which indicates that the probe molecules conjugated structure is not destroyed, it may be that ozone only reacts with the terminal ethylenic bond, causing the ether bond to break (Fig. 2).



Scheme 1 Synthesis of BCT. **a** MeOH, HOAc, 0 °C, 5 h; **b** EtOH, NaOH, HCl , room temperature, 2 h; **c** 4-bromobut-1-ene, DMF, K_2CO_3, 70 °C, 24 h

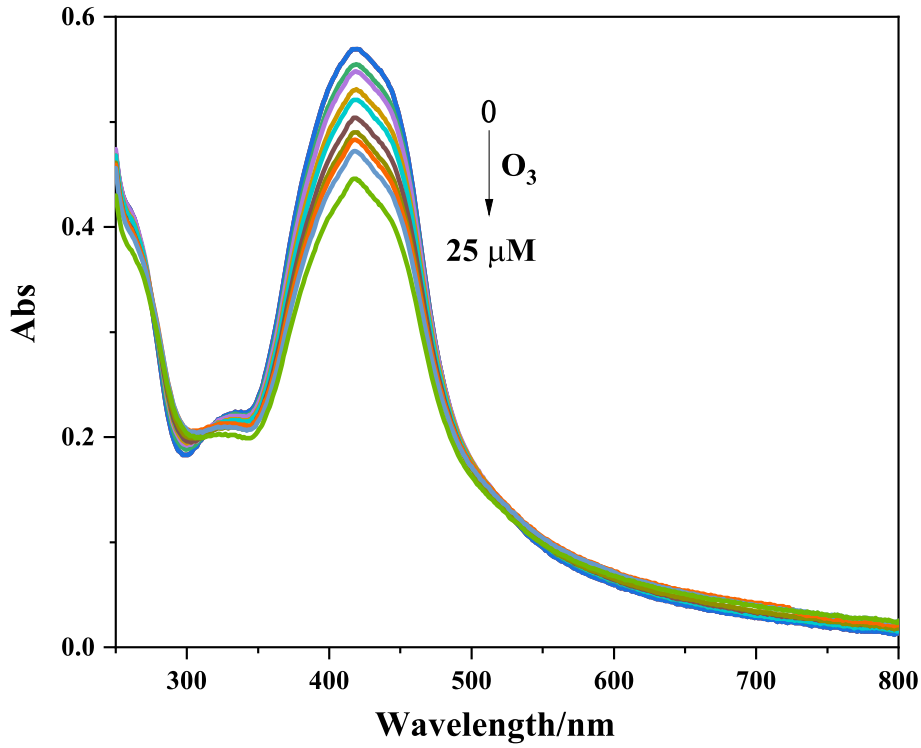


Fig. 1 Comparison of UV absorption before and after the reaction of BCT and O_3

As shown in Fig. 3a fluorescence spectrum experiment, BCT showed weak fluorescence in PBS buffer. In the PBS buffer solution at pH=7.4, with the increase of O_3 concentration, the fluorescence intensity of BCT at 550 nm (λex = 425 nm) was significantly enhanced. We believe that the increase in fluorescence intensity is due to the break of the ether bond leading to the interruption of the photoinduced electron transfer (PET) process. When the O_3 concentration reaches 25 μM, the fluorescence intensity reaches the plateau. The fluorescence intensity of BCT showed a good linear relationship in the range of O_3 concentrations of 0 to 25 μM (Fig. 3b). According to the detection limit formula LOD = 3σ/k (Where σ is the standard deviation of the blank sample measurement, k is the slope between fluorescence intensity and O_3 concentration) (Zhao et al. 2020), the minimum detection concentration is calculated to be 43 nM, which indicates that the probe can be used to detect trace amounts of O_3 in a physiological environment.

Study on response performance of BCT

To further study the stability of the probe BCT under different pH conditions, we conducted relevant fluorescence response experiments. As can be seen from Fig. 4, when no O_3 aqueous solution was added, the probe BCT showed weak fluorescence emission in the range of pH 6.0 to 8.0. When 25 μM O_3 aqueous solution was added, the BCT showed a fluorescence enhancement in

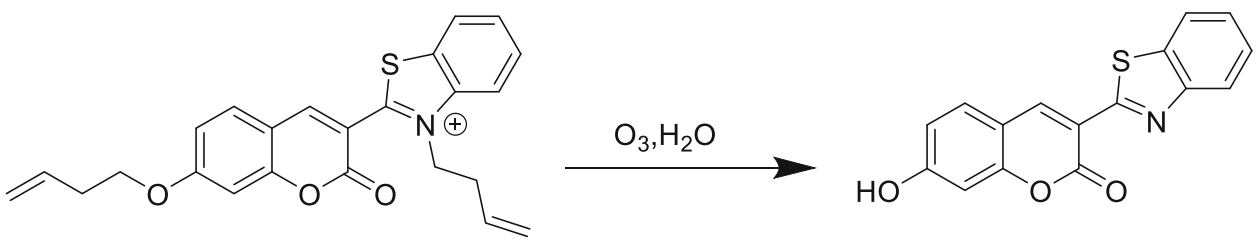


Fig. 2 Comparison of the structure of probe BCT and O_3 before and after the reaction

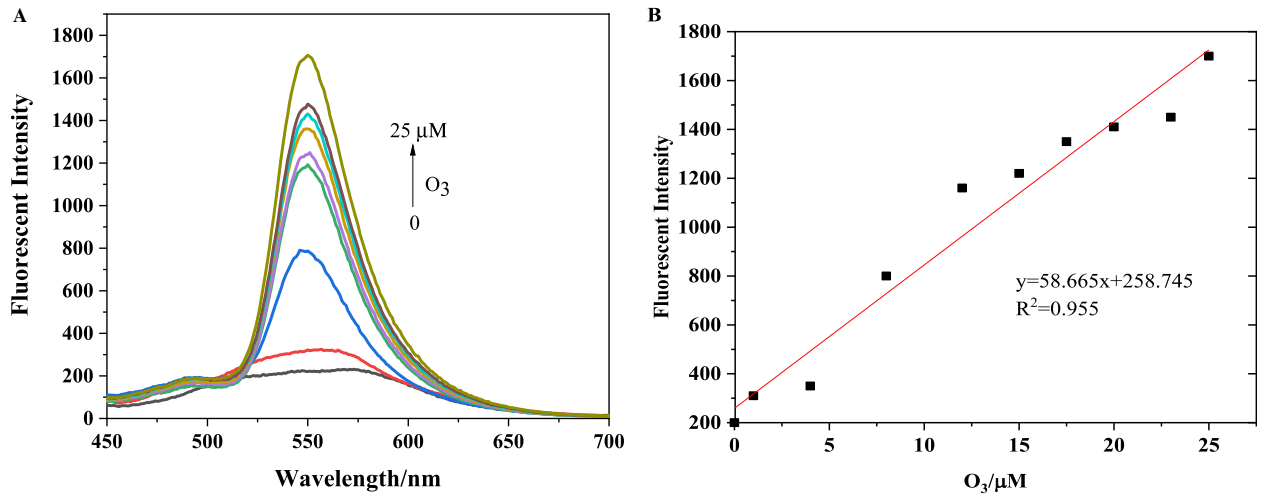


Fig. 3 Fluorescence spectrum change curve. **a** The spectrum of probe BCT (10 μM) when different concentrations of O_3 aqueous solution were added to PBS buffer (pH =7.4, 10 mM). **b** Linearly fit the fluorescence spectrum and calculate its minimum detection limit

the pH range of 6 to 8, and there is no obvious difference in the degree of fluorescence enhancement at different pH. This indicates that the probe is very stable in detecting O_3 in a neutral environment, which indicates that the field of biosensing has a good foundation.

Response time is an important factor to evaluate the performance of fluorescent probes. To explore the reaction performance of BCT and O_3, we used fluorescence spectroscopy to investigate the response time of the probe with 2.5 times the amount of O_3. Plot the fluorescence intensity of the BCT probe at 550 nm peak as a function of time. As shown in Fig. 5, the fluorescence intensity can be increased to the highest within 20 min, basically reaching plateau, which shows that the probe can complete the detection of ozone in aqueous solution in a short time.

Study on the selectivity of BCT

A probe has good selectivity for a specific analyte, which determines whether the probe can specifically recognize the analyte. This article selects common cations, active oxygen, and amino acids, including 1: blank; 2: Na^+; 3: K^+; 4: Ca^{2+}; 5: Cu^{2+}; 6: Fe^{3+}; 7: $ONOO^-$; 8: H_2O_2; 9: $O_2{\bullet}^-$; 10: ClO^-; 11: $^1O_2$; 12: ·OH; 13: NO; 14: TBHP; 15:

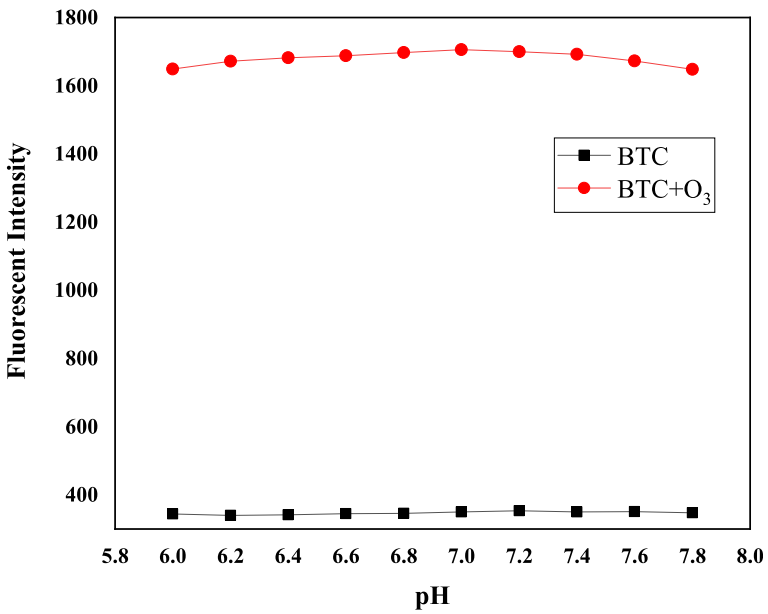


Fig. 4 Response of probe BCT (10 μM) to O_3 (25 μM) under different pH conditions

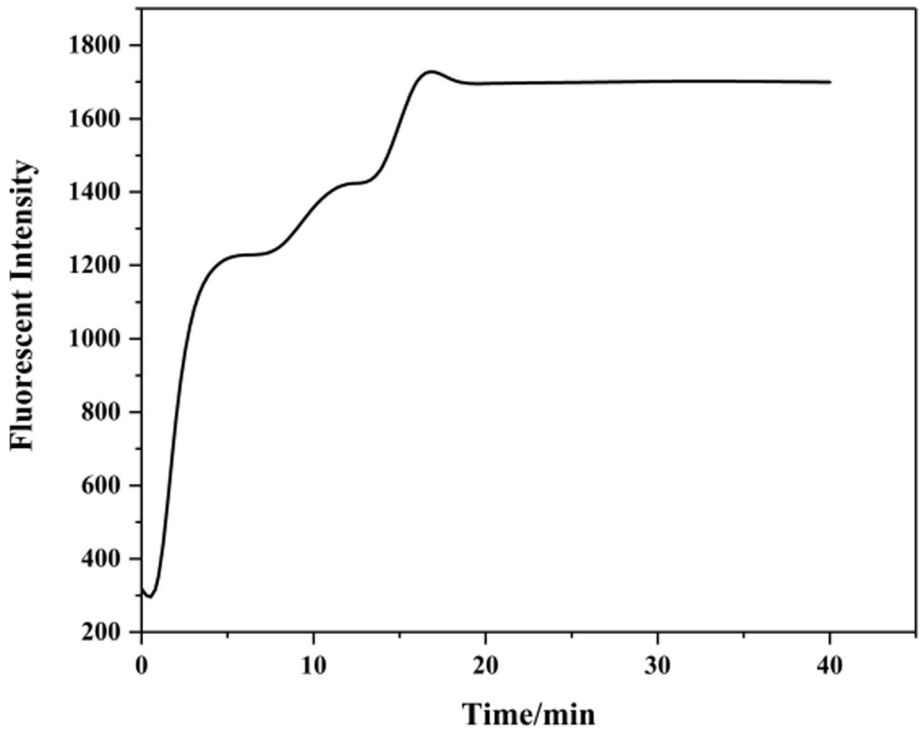


Fig. 5 Fluorescence response time of 10 μM BCT in PBS buffer (10 mM, pH 7.4) to 25 μM O_3 aqueous solution

GSH; 16: Cys; 17: O_3. The analyte concentration is 25 μM. Figure 6a shows the specific fluorescence response of BCT to O_3 in PBS buffer. Various analytes were added to the PBS buffer solution of the probe BCT, and then the fluorescence intensity at 550 nm was recorded. The test results show that the probe BCT has a specific selectivity for O_3 and hardly reacts to other cations, reactive oxygen species, and amino acids. In the presence of various analytes, the fluorescence color of the probe BCT appears green fluorescence only in the presence of O_3 (Fig. 6b). This result confirms that the probe BCT can be used as a specific fluorescent probe for detecting O_3.

Research on reaction mechanism

According to the previous research results (Nam et al. 2016), we further deduced the possible mechanism of the interaction between the probe BCT and ozone. The structure of the probe was verified by HRMS and ^{1}H NMR. As shown in Fig. 7, in the probe BCT, coumarin and benzothiazole are used as signal groups, and the terminal ethylenic bond of the coumarin part is a potential O_3 reaction site and also an electron acceptor, which happens to form a PET process with the electron-donor benzothiazole group. Due to the effect of PET, the fluorescence of the probe itself is weak. However, after the addition reaction between the terminal ethylenic bond of the probe BCT and ozone, formaldehyde and hydrogen peroxide molecules are released, and the β-elimination reaction occurs by itself. The ethylenic bond is broken, which causes the PET process to be interrupted and fluorescence is restored. This can just explain the fluorescence phenomenon after the probe BCT reacts with ozone.

Conclusions

A new water-soluble fluorescent probe BCT was synthesized by a substitution reaction of 4-bromo-1-butene and hydroxycoumarin derivatives, which can detect ozone in aqueous solution. The structure of the probe BCT was confirmed by NMR and HRMS characterization, which indirectly verified its mechanism of action. The substitution reaction of 4-bromo-1-butene with the phenolic hydroxyl group of the coumarin derivative removes one molecule of HBr to form a weakly fluorescent probe molecule BCT. According to the specific reaction between ozone and terminal olefin, through the process of ozone cyclization, β-elimination, and intermediate hydrolysis, coumarin derivatives with strong fluorescence are obtained. We conducted further research on it and found that the probe has excellent performances such

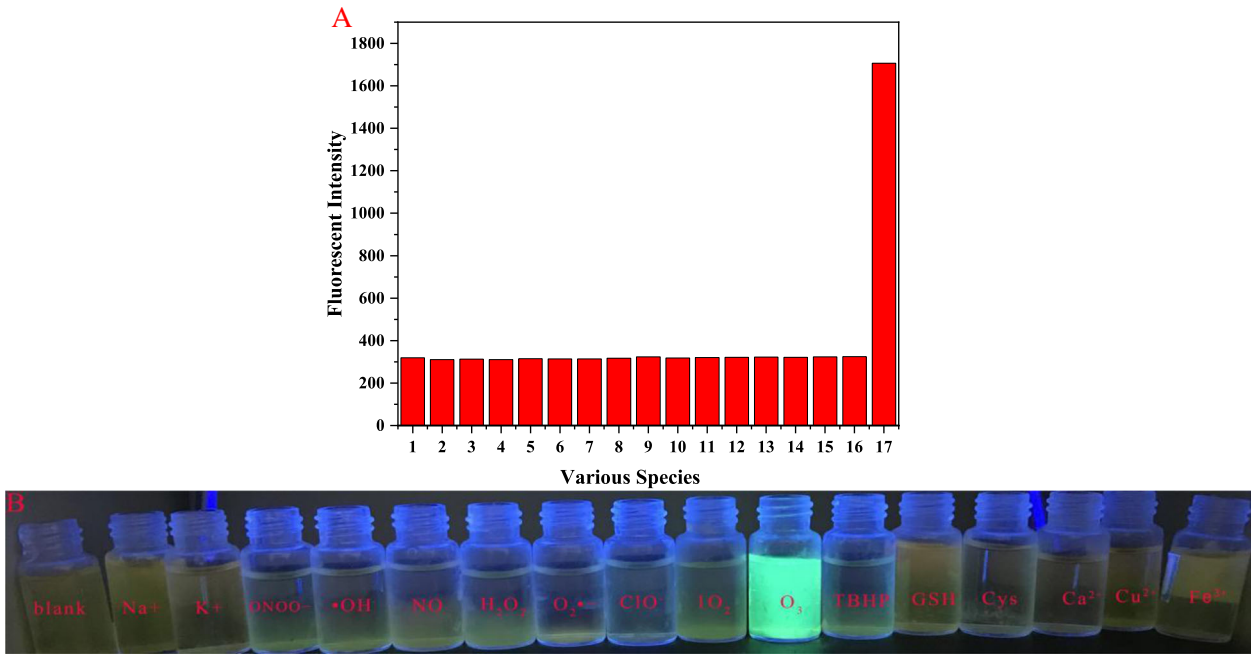


Fig. 6 a Fluorescence intensity change of the probe BCT (10 μM) in PBS aqueous buffer (10 mM, pH=7.4) after reacting with each analyte. **b** Probe BCT (10 μM) at O_3 (1.0 equivalent) and other anions (10.0 equivalents) in PBS solution (pH=7.4, 10 mM) under the ultraviolet light fluorescence photo

as high sensitivity, strong specificity, and fast response speed. Through the fluorescence experiment, the effect of O_3 on the probe can be completed within 20 min, the fluorescence intensity is significantly enhanced, and the detection limit is as low as 43 nM. More importantly, the probe shows super stability under weak alkali and acidic environment, which provides the necessary conditions for its detection of O_3 in physiological systems.

Availability of data and materials

All experiments were conducted in the School of Chemistry and Food Engineering, Changsha University

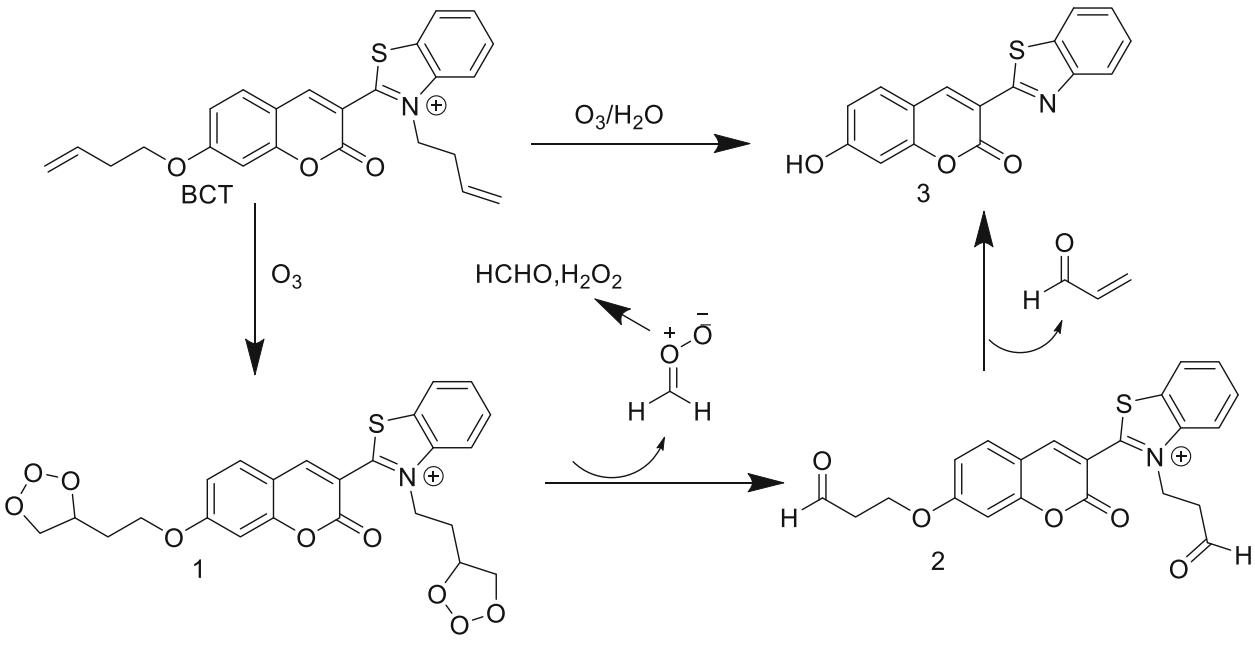


Fig. 7 The reaction mechanism of probe BCT and O_3

of Science and Technology, Hunan, China. All data can be obtained from the corresponding author (Professor Li Heping) of the manuscript. Research data has been provided in the manuscript and supporting information files.

Abbreviations

O_3: Ozone; BCT: 3-(but-3-en-1-yl)-2-(7-(but-3-en-1-yloxy)-2-oxo-2H-chromen-3-yl)benzo[d]thiazol-3-ium; LOD: Detection limit; PET: Photo-induced electron transfer; IDs: Indigo-5, 5-disulfonate; BDD: Boron-doped diamond; PBS: Phosphate buffered saline; ROS: Reactive oxygen species; H_2O_2: Hydrogen peroxide; NaClO: Sodium hypochlorite; TBHP: Tert-butyl hydroperoxide; $O_2^{\bullet-}$: Superoxide anion radical; KO_2: Potassium peroxide; DMSO: Dimethyl sulfoxide; $^1O_2$: Singlet oxygen; •OH: Hydroxyl radical; Fe(II)EDTA: Sodium iron ethylenediaminetetraacetate; UV-vis: Ultraviolet absorption spectrum; TMS: Tetramethylsilane; ^{1}H NMR: Hydrogen nuclear magnetic resonance; HRMS: High-resolution mass spectrum; DMF: Dimethylformamide; K_2CO_3: Potassium carbonate; EtOAc: Acetic acid; Na_2SO_4: Sodium sulfate; ^{13}C NMR: Carbon nuclear magnetic resonance; $COCl_3$: Deuterated chloroform; NaOH: Sodium hydroxide; HCl: Hydrogen chloride; MeOH: Methanol; EtOH: Ethanol; Na^+: Sodium ion; K^+: Potassium ion; Ca^{2+}: Calcium ion; Cu^{2+}: Copper ions; Fe^{3+}: Iron ion; $ONOO^-$: Peroxynitrite anion; H_2O_2: Hydrogen peroxide; ClO^-: Hypochlorite ion; NO: Nitric oxide; GSH: Glutathione; Cys: Cysteine; HBr: Hydrogen bromide

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40543-021-00269-3.

Additional file 1 The following information is available in the supplementary material: Synthesis method of probe BCT and its intermediates; HRMS spectrum of probe BCT (**Figure S1**); ^{1}H NMR spectrum of probe BCT in CDCl3 (**Figure S2**); ^{13}C NMR spectrum of probe BCT in CDCl3 (**Figure S3**).

Acknowledgements

Not applicable.

Authors' contributions

CZ synthesized the probe BCT. YL and JS were mainly responsible for the characterization of BCT. KC was responsible for data collection and analysis and article writing. HL was the corresponding author. All authors read and approved the final manuscript.

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Availability of data and materials

All data generated or analyzed during this study are included in this published article and its supplementary information files.

Declarations

Competing interests

The authors declare that they have no competing interests.

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