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Fluorescent probe based on EDOT derivative EDOT-EN: Highly selective detection of biogenic amine Cadaverine and its application in food freshness monitoring

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Abstract

Biogenic amines, which are indicators, can be used to rapidly assess food spoilage. In this study, EDOT derivatives, **EDOT-EN₁**, **EDOT-EN₂**, **EDOT-EN₃** and **EDOT-EN₄** were prepared as probe for the detection of biogenic amines. The four fluorescent probes were prepared by introducing different substituents based on 3,4-ethylenedioxythiophene. After conducting tests on their photophysical properties and making comparisons, it was found that the effect of **EDOT-EN₁** was better among the four compounds. Compared with **EDOT-EN₂** and **EDOT-EN₃**, **EDOT-EN₁** and **EDOT-EN₂** exhibited weaker fluorescence under solvent conditions. In practical applications, they were difficult to locate and determine the existence state, which would result in excessive usage and cause harm to the environment itself, thus being eliminated. Compared with **EDOT-EN₁**, the time required for the response completion of **EDOT-EN₂** was only slightly different. However, during the titration process, the fluorescence change in response to the increase amount was unstable and insensitive, unable to achieve good quantitative detection of the detected substance, and its titration upper limit was approximately 1.5 times higher than that of **EDOT-EN₁**. Therefore, further testing and research were conducted on **EDOT-EN₁**. The probe can achieve

detection of 1,5-pentanediamine (Cad) due to the aza-Michael addition reaction between **EDOT-EN₁** and Cad, forming Schiff base compounds as products. Furthermore, EDOT can be prepared as a portable test paper that is responsive to Cad, which can detect the freshness of shrimp and fish. Furthermore, an electrospun film doped with **EDOT-EN₁** has been prepared, which can selectively detect Cad vapour.

Keywords: Biogenic amines; Fluorescence probe; test paper; vapor detection

1. Introduction

Biogenic amines(Bas) represent a class of nitrogenous, small-molecule compounds.^[1] These compounds are produced by decarboxylation of amino acids or amination of aldehydes.^{[2][3]} They are widely present in the metabolic systems of foods, organisms and microorganisms.^{[4][5][6][7]} Biogenic amines are classified into two distinct categories: monoamines^[8] and polyamines^{[9][10][11][12]}. Monoamines include Cad, putrescine, tyramine, histamine, tryptamine and 2-phenylethylamine. Cad, a typical biogenic amine, is an important marker of meat and dairy product spoilage in the field of food science.^{[13][14]} Its over-accumulation may lead to histamine toxicity syndrome, which manifests itself in the form of headache, vomiting and even anaphylactic shock.^[15] Conversely, low concentrations of Cad have been observed to promote cell growth,^[16] possibly by modulating membrane permeability or acting as a signaling molecule involved in metabolic pathways. Its dual biological properties (physiological function and toxicity) make it a hotspot for multidisciplinary research. The subject of food safety is one of constant concern, yet a plethora of food safety incidents continue to be reported.^{[17][18]} Spoiled food can contain elevated levels of toxic substances, and accidental ingestion of spoiled food can cause a range of adverse reactions ^[19], including nausea and diarrhea. Consequently, the development of a straightforward and expeditious technique for evaluating the freshness of Cad is of paramount importance in the prevention of diseases.

There are a large number of traditional methods available for identifying Cad in liquids.^{[20][21]} These encompass mass spectrometry^[22], Raman spectroscopy^[23], and capillary electrophoresis techniques, amongst others. However, these methods are

characterized by prolonged analysis times, complexity, and limited selectivity. Conversely, the utilization of fluorescent probes as a novel detection method offers distinct advantages^[24], including simplicity in operation, high sensitivity, and high selectivity^[25]. A plethora of methods have been developed for the detection of Cad^{[26][27][28]}; however, the preparation of a fluorescent probe for the detection of Cad based on the thiophene derivative EDOT as a parent ring has not been reported. Nanofibrous membranes prepared by electrostatic spinning offer distinct advantages^[29], including small diameter and large specific surface area^[30], which position them as optimal materials for thin-film sensing applications^[31]. However, there is a paucity of reports on the combination of fluorescent probes with electrostatic spinning technology for Cad detection^{[32][33]}. Consequently, there is a significant research opportunity to develop a thin film with high selectivity and rapid detection characteristics for Cad.

Therefore, via the Suzuki-Miyaura coupling, we employed 4-(N, N-dimethylamino) phenylboronic acid pinacol ester, 4-aminophenylboronic acid pinacol ester, 4-hydroxyphenylboronic acid pinacol ester, and 4-biphenylboronic acid pinacol ester as electron-donating precursors, with ethyl cyanoacetate as the electron-accepting moiety, to synthesize four novel fluorescent probes (**EDOT-EN₁-EDOT -EN₄**). Among these, **EDOT-EN₁** exhibited superior photophysical properties and was selected for comprehensive characterization. This probe demonstrates excellent selectivity and rapid response toward Cad, with fluorescence intensity at 508 nm showing a linear correlation with Cad concentration. Furthermore, **EDOT-EN₁** was successfully fabricated into portable test strips and electrospun films, enabling specific detection of gaseous Cad and visual assessment of food freshness through distinct fluorescence color changes.(被动语态)

2. Experimental

2.1. Materials and instruments

If not specified, the chemical reagents used in the experiment are from commercial companies without further purification. Main chemical reagents, instruments see in the

Supporting information.

2.2. Synthesis of **EDOT-EN**

In a dry solane-shaped bottle, 2-(3, 4-vinyl dioxythiophene) formaldehyde (11.75 mmol, 2.0 g) was added and completely dissolved in acetonitrile at 0 °C. Then, N-bromobutanamide (NBS, 12.92 mmol, 2.3 g) was added. React at room temperature (RT, approximately 25 °C) for 60 hours. After the reaction is completed, the reaction solution is poured into 200 mL of ice H₂O, extracted with dichloromethane (3×50 mL), combined with the organic phase, washed with saturated brine (2×50 mL), dried with anhydrous sodium sulfate, filtered, and the solvent is removed by vacuum distillation to obtain the crude product. The crude product was separated and purified by silica gel column chromatography (petroleum ether: ethyl acetate / 15:1), and compound **2** was obtained, which was a white solid.

Compound **2** (1.0 mmol, 249.07 mg), ethyl cyanoacetate (1.2 mmol, 135.73 mg), Piperidine (0.2 equiv), and CH₃COOH (200 µL) were placed in a pressure-resistant tube. Then add 7 mL of acetonitrile. React in an oil bath at 100 °C for 3 hours. After the reaction was completed, the red solid compound **3** was obtained by column chromatography purification with dichloromethane and methanol (8:1) as eluents through rotary distillation.

Compound **3** (2 mmol, 688.25 mg), 4-(N, N-dimethylamino) phenylboronic acid pinacol ester (2.0 mmol, 494.28 mg) [1,1'-Bis(diphenylphosphino) ferrocene] dichloropalladium (II) (0.4 mmol, 292.42 mg) was placed in a pressure-resistant tube, and then 7 mL Dio was added. Dissolve K₂CO₃ (4.0 mmol, 552.84 mg) in 0.5 mL of H₂O and add it to the system. React in an oil bath at 80 °C in an N₂ environment for 24 hours. After the reaction is completed, cool to room temperature, pour the reaction solution into 200 mL of ice H₂O, extract with ethyl acetate (3×50 mL), combine the organic phase, wash with saturated brine (2×50 mL), dry with anhydrous sodium sulfate, filter, and remove the solvent by vacuum distillation to obtain the crude product. The crude product was separated and purified by silica gel column chromatography (petroleum ether: ethyl acetate / 12:1), and compound **EDOT-EN₁** was obtained, which

was a pale-yellow solid.

Compound **3** (2 mmol, 688.25 mg), 4-Aminophenylboronic acid pinacol (2 mmol, 438.18 mg) [1,1'-Bis(diphenylphosphino) ferrocene] dichloropalladium (II) (0.4 mmol, 292.42 mg) was placed in a pressure-resistant tube, and then 7 mL Dio was added. Dissolve K₂CO₃ (4 mmol, 552.84 mg) in 0.5 mL of H₂O and add it to the system. React in an oil bath at 80 °C in an N₂ environment for 24 hours. After the reaction is completed, cool to room temperature, pour the reaction solution into 200 mL of ice H₂O, extract with ethyl acetate (3×50 mL), combine the organic phase, wash with saturated brine (2×50 mL), dry with anhydrous sodium sulfate, filter, and remove the solvent by vacuum distillation to obtain the crude product. The crude product was separated and purified by silica gel column chromatography (petroleum ether: ethyl acetate / 3:1), and compound **EDOT-EN₂** was obtained, which was a red solid.

Compound **3** (2 mmol, 688.25 mg), 4-Hydroxyphenylboronic acid pinacol ester (2 mmol, 440.14 mg) [1,1'-Bis(diphenylphosphino) ferrocene] dichloropalladium (II) (0.4 mmol, 292.42 mg) was placed in a pressure-resistant tube, and then 7 mL Dio was added. Dissolve K₂CO₃ (4 mmol, 552.84 mg) in 0.5 mL of H₂O and add it to the system. React in an oil bath at 80 °C in an N₂ environment for 24 hours. After the reaction is completed, cool to room temperature, pour the reaction solution into 200 mL of ice H₂O, extract with ethyl acetate (3×50 mL), combine the organic phase, wash with saturated brine (2×50 mL), dry with anhydrous sodium sulfate, filter, and remove the solvent by vacuum distillation to obtain the crude product. The crude product was separated and purified by silica gel column chromatography (petroleum ether: ethyl acetate / 6:1), and compound **EDOT-EN₃** was obtained, which was a red solid.

Compound **3** (1 mmol, 344.12 mg), 4-Methylphenylboronic acid pinacol ester (1 mmol, 280.17 mg) [1,1'-Bis(diphenylphosphino) ferrocene] dichloropalladium (II) (0.2 mmol, 146.21 mg) was placed in a pressure-resistant tube, and then 7 mL Dio was added. Dissolve K₂CO₃ (2 mmol, 276.42 mg) in 0.5 mL of H₂O and add it to the system. React in an oil bath at 80 °C in an N₂ environment for 24 hours. After the reaction is completed,

cool to room temperature, pour the reaction solution into 200 mL of ice H₂O, extract with dichloromethane (3×50 mL), combine the organic phase, wash with saturated brine (2×50 mL), dry with anhydrous sodium sulfate, filter, and remove the solvent by vacuum distillation to obtain the crude product. The crude product was separated and purified by silica gel column chromatography (petroleum ether: ethyl acetate / 5:1), and compound **EDOT-EN₄** was obtained, which was a yellow solid.

The nuclear magnetic characterization of the corresponding products was ¹H NMR /¹³C NMR and HR-MS (Fig. S1-S10).

2.3 General Information for Spectroscopic Studies

Prepare probe (**EDOT-EN₁**) stock solution (1 mM) and Cad stock solution (10 mM) in ethanol (EtOH) to be prepared using PBS buffer solution. For the titration experiment, a certain amount of Cad stock solution was added to the EtOH-PBS (7:3) solution containing a fixed amount of **EDOT-EN₁** (20 μL). For selective and competitive experiments, all analytes were prepared in distilled water solutions and tested in ethanol-PBS (7:3). Before recording all spectral tests, shake the test solution thoroughly with the analyte.

2.4 Preparation of Probe **EDOT-EN₁** test strips and their application

Soak the filter paper (1cm²) in the stock solution of **EDOT-EN₁** for 15 minutes. After soaking, place the filter paper in an oven at 50 °C to dry, and then cut it into uniform sizes (1/4 cm²). For different solutions (400 μM, 1. Blank; 2. MgCl₂; 3. ZnSO₄; 4. CuCl₂; 5. K₃PO₄; 6. H₂O₂; 7. FeSO₄; 8. NaClO; 9. NaNO₂; 10. Monoethanolamine; 11. Benzylamine; 12. Ditridecylamine; 13. L-Arg; 14. L-Cys; 15. Hcy; 16. Furfurylamine; 17. Dimethylamine; 18. Dibutylamine; 19. Triethylamine; 20. Cad) is used for inspection. Take a drop from different solutions with a dropper and add it to the cut test paper. After reacting for two hours, observe it under a fluorescent lamp and a UV lamp respectively.

The prepared test strips were respectively placed in two groups of petri dishes containing fish and shrimp. One group of fish and shrimp was put into a refrigerator at

-8 °C, while the other group was placed as a control group in a room at room temperature (about 15 °C). Observe the color changes of the test strips under fluorescent lamps and ultraviolet lamps respectively.

2.5 Preparation and detection application of probe **EDOT-EN₁** spinning film

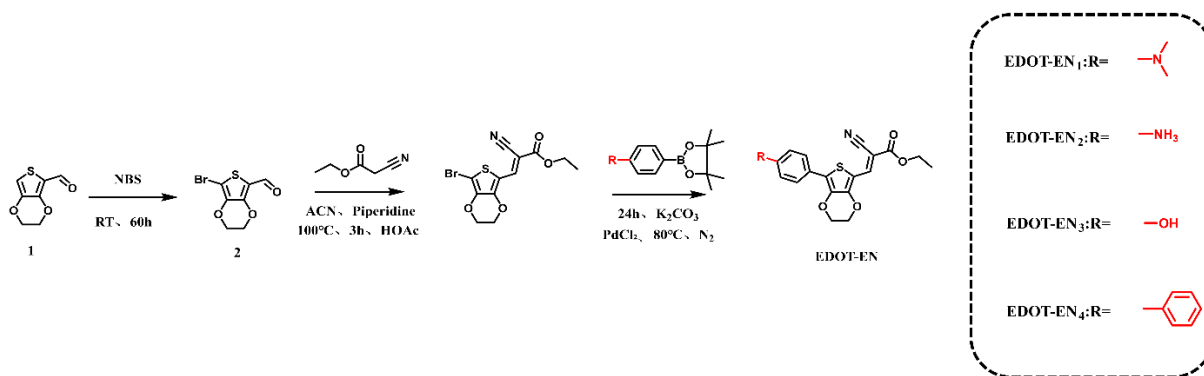
Mix **EDOT-EN₁** (3.8 μg), polyurethane (HDW-3020) (2 g) and N, N-dimethylformamide (DMF) (6 g) evenly and draw them into the needle tube. The spinning film is formed after 5 hours using an electrospinning machine. Immerse the cut 1×2cm rectangular spinning film in 400 mM of various interfering solutions. After soaking 12 hours, observe the color change of the spun film under natural light and a 365nm handheld ultraviolet lamp.

Put 2 ml of the same concentration (400 mM) of different interfering substance (1. Blank; 2. Cad; 3. H₂O₂; 4. Diethylamine 5. Triethylamine 6. 2-furfuramine; 7. 2-furanamine 8. Pyridine; 9. Trimethylamine; 10. Butylamine 11. Histamine; 12. Propylamine; 13. Benzylamine 14. Arginine; 15. Cysteine; 16. Glutathione 17. Na₂S; 18. NaHS.) solutions into 2 ml of bullet heads, soak 0.5 x 1 cm of spinning membranes for 12 hours, and observe the corresponding conditions of the spinning membranes in different interfering substance solutions.

In additional, put 2 ml of Cad solution of different concentrations (0, 100, 200, 400 mM) into a 10 ml glass bottle, fix a 0.5 × 1 cm spinning membrane on top of it, and place it in a 45 °C water bath at a constant temperature for 40 minutes. Then observe the fluorescence difference of the membrane under sunlight and ultraviolet lamp.

3. Results and discussion

The synthesis of the probe **EDOT-EN** is illustrated in Scheme 1. The corresponding products were characterized by ¹H NMR, ¹³C NMR, and HR-MS (Fig. S1–S7).



Scheme 1. The synthesis route for the probe **EDOT-EN**.

As shown in Scheme 1, we designed four probes (**EDOT-EN₁–EDOT-EN₄**) featuring EDOT as the π -bridge, ethyl cyanoacrylate as the electron acceptor, and varied electron-donating groups (N, N-dimethylamino for **EN₁**, amino for **EN₂**, hydroxyl for **EN₃**, and phenyl for **EN₄**). All derivatives operate via a reactive ICT-off color-switching mechanism, wherein the nucleophilic addition–elimination of Cad cleaves the strong electron-withdrawing cyanoacrylate unit, disrupts the D- π -A push-pull equilibrium, enlarges the HOMO-LUMO gap, and triggers a pronounced blue shift.

3.1 Photophysical properties

Stock solutions (1 mM) of **EDOT-EN₁**, **EDOT-EN₂** and **EDOT-EN₃** were prepared in DMSO; **EDOT-EN₄** required THF owing to its limited solubility.

Add 20 μ L of the probe stock solution to 2 ml of different solvents and conduct optical tests. Photophysical characterization in diverse solvents (Fig. S14a-c) revealed absorption maxima in EtOH at 526, 480, 444, and 430 nm for **EN₁–EN₄**, respectively.

To bridge the gap between laboratory spectroscopy and real-world detection, we prioritized biocompatibility, environmental safety, and field-deployability while preserving adequate spectral response, and therefore selected the EtOH/H₂O system for subsequent assays.

Subsequently, 20 μ L of the probe solution was added into 2 mL of various solvents for UV-Vis spectroscopic measurements. The photophysical characterization in different solvents (Figures S14a-S14d) reveals that the maximum absorption wavelengths of **EDOT-EN₁**, **EDOT-EN₂**, **EDOT-EN₃**, and **EDOT-EN₄** in EtOH are 526, 480, 444, and 430 nm, respectively. Such differences mainly arise from the distinct

electron-donating R groups.

The -NMe₂ group is a strong electron-donating group, which forms a strong donor–acceptor (D-A) system with the electron-withdrawing cyano group on the molecular core, giving rise to an obvious intramolecular charge transfer (ICT) transition. The ICT state possesses a large transition dipole moment, which lowers the excited-state energy. Meanwhile, the steric hindrance of the methyl groups restricts rotation around the C-N bond, allowing the lone-pair electrons on the nitrogen atom to participate more effectively in p- π conjugation with the benzene ring, thus leading to a significant red shift in absorption. The -NH₂ group is also a strong electron-donating group, but its absorption maximum is shorter than that of **EDOT-EN₁**. This is because the N-H bond can form intermolecular hydrogen bonds, especially in EtOH, which reduces the contribution of the nitrogen lone pair to p- π conjugation with the benzene ring. The -OH group is a moderate electron-donating group with weaker electron-donating ability. A weaker ICT effect results in a higher excited-state energy and a correspondingly blue-shifted absorption. The -Ph group is a weak electron donor. Although it extends the π -conjugated system, it lacks strong electron-donating character and thus induces a weak ICT effect, corresponding to the shortest absorption wavelength among the four probes.

According to Figs. S14a-d, the UV-vis absorption spectra of **EDOT-EN₁**, **EDOT-EN₂**, **EDOT-EN₃**, and **EDOT-EN₄** were measured in various solvents. All four probes exhibit solvent-polarity-dependent absorption behavior, showing stable and sharp characteristic absorption peaks in organic solvents. And then, according to the fluorescence behavior of **EDOT-EN₁**, **EDOT-EN₂**, **EDOT-EN₃**, and **EDOT-EN₄** in various solvents (Fig 1.), all four probes exhibit nice fluorescence performance in EtOH, which further validates the feasibility of the selected EtOH/H₂O system for subsequent detection.

It can be observed that the fluorescence intensities of the four probes in EtOH follow the order: **EDOT-EN₁** > **EDOT-EN₂** >> **EDOT-EN₃** > **EDOT-EN₄**. Their emission wavelengths decrease in the sequence: **EDOT-EN₁** (620 nm) > **EDOT-EN₂**

(600 nm) > **EDOT-EN₃** (540 nm) > **EDOT-EN₄** (520 nm) (Fig 1.).

EDOT-EN₁ shows the highest fluorescence intensity (~900 a.u.) and the longest emission wavelength (~620 nm) in EtOH (Fig 1.a), accompanied by a distinct red shift. This is mainly attributed to three mechanisms: Intramolecular charge transfer (ICT) effect. The dimethylamino group (-NMe₂) acts as a strong electron donor, whose lone-pair electrons on the N atom couple efficiently with the benzene ring via p- π conjugation, constructing a strong donor-acceptor system with the electron-withdrawing ester-cyano core. A pronounced ICT transition occurs in the excited state, generating a charge-separated state with a large dipole moment and markedly lowering the excited-state energy, leading to significant red shifts in both absorption and emission. Solvation stabilization effect. As a highly polar protic solvent, EtOH stabilizes the ICT excited state through dipole-dipole interactions, further lowering the S₁ energy level and enlarging the Stokes shift. Meanwhile, intermolecular hydrogen bonds form between EtOH and the ester/cyano groups, enhancing molecular rigidity and suppressing nonradiative decay. Aggregation-induced emission (AIE) characteristic. The steric hindrance of -NMe₂ restricts intramolecular rotation (RIR), reducing energy dissipation via molecular motions in the excited state and thus significantly improving the fluorescence quantum yield. In addition, EtOH may act as a poor solvent to induce molecular aggregation, further boosting the AIE effect.

EDOT-EN₂ exhibits moderate fluorescence intensity (~550 a.u.) and a relatively long emission wavelength (~600 nm) in EtOH (Fig 1.b). Although its emission is obviously blue-shifted and the intensity is reduced by approximately 40% relative to **EDOT-EN₁**, its fluorescence performance remains superior to that of the other probes. Compared with **EDOT-EN₁**, the differences arise mainly from: Electron-donating ability. Although -NH₂ is also an electron-donating group, the +I inductive effect of H is weaker than that of methyl groups, and the p- π conjugation between its lone-pair electrons and the benzene ring is less efficient than that of -NMe₂. More importantly, -NH₂ acts as a hydrogen-bond donor and forms N-H $\cdots$ O hydrogen-bond networks with EtOH, which partially trap the nitrogen lone pair and weaken the +M conjugative effect,

resulting in lower ICT efficiency. Hydrogen -bonding competition effect. The hydrogen-bonding interaction between -NH₂ and EtOH exerts dual influences: on one hand, it enhances intermolecular interactions and may promote AIE; on the other hand, solvation competitively stabilizes the ground state, increases the energy gap between the ground state and the ICT excited state, and reduces the population of the ICT state, leading to decreased fluorescence intensity and a blue-shifted emission relative to **EN₁**. Diversified excited-state decay pathways. Hydrogen-bond networks may introduce additional vibrational relaxation channels, facilitating nonradiative decay of the excited state and further lowering the fluorescence quantum yield.

EDOT-EN₃ displays drastically reduced fluorescence intensity (~35 a.u.) and an obviously blue-shifted emission (~540 nm) in EtOH (Fig 1.c), together with unique solvent dependence (stronger emission in DMSO than in EtOH). The poor fluorescence performance is mainly ascribed to the hydroxyl group (-OH), which serves as both a strong hydrogen-bond donor and acceptor and forms extensive intermolecular hydrogen-bond networks with EtOH. Such strong interactions introduce an excited-state intramolecular proton transfer (ESIPT) pathway, providing an efficient nonradiative decay channel and significantly decreasing the fluorescence quantum yield. Moreover, the high electronegativity of oxygen weakens the p- π conjugation between its lone-pair electrons and the benzene ring, and the -I inductive effect partially counteracts the +M conjugative effect, resulting in weaker overall electron-donating ability. Notably, unlike **EDOT-EN₁** and **EDOT-EN₂**, **EDOT-EN₃** exhibits stronger fluorescence in DMSO (an aprotic solvent) than in EtOH. This is because DMSO cannot act as a hydrogen-bond donor and thus cannot form strong hydrogen-bond networks with -OH, which suppresses the ESIPT quenching pathway and partially restores fluorescence emission. This observation clearly confirms the decisive role of hydrogen bonding in the photophysical behavior of **EN₃**.

EDOT-EN₄ shows the lowest fluorescence intensity (~25 a.u.) and the shortest emission wavelength (~520 nm) in EtOH (Fig 1.d), and its emission is insensitive to solvent polarity. This is mainly because the phenyl group (-Ph) is a weak electron donor:

its π electrons conjugate with the molecular core but fail to provide sufficient electron density to form an effective ICT state. Second, due to the absence of a large dipole moment change in the ICT state, the excited state is insensitive to solvent polarity, and the high polarity of EtOH does not provide significant stabilization. Furthermore, the planar rigid structure of -Ph facilitates intermolecular π - π stacking, which tends to form excimers or induce nonradiative energy transfer in the aggregated state, thereby reducing luminescence efficiency-contrary to the AIE effect, which accounts for its extremely weak emission.

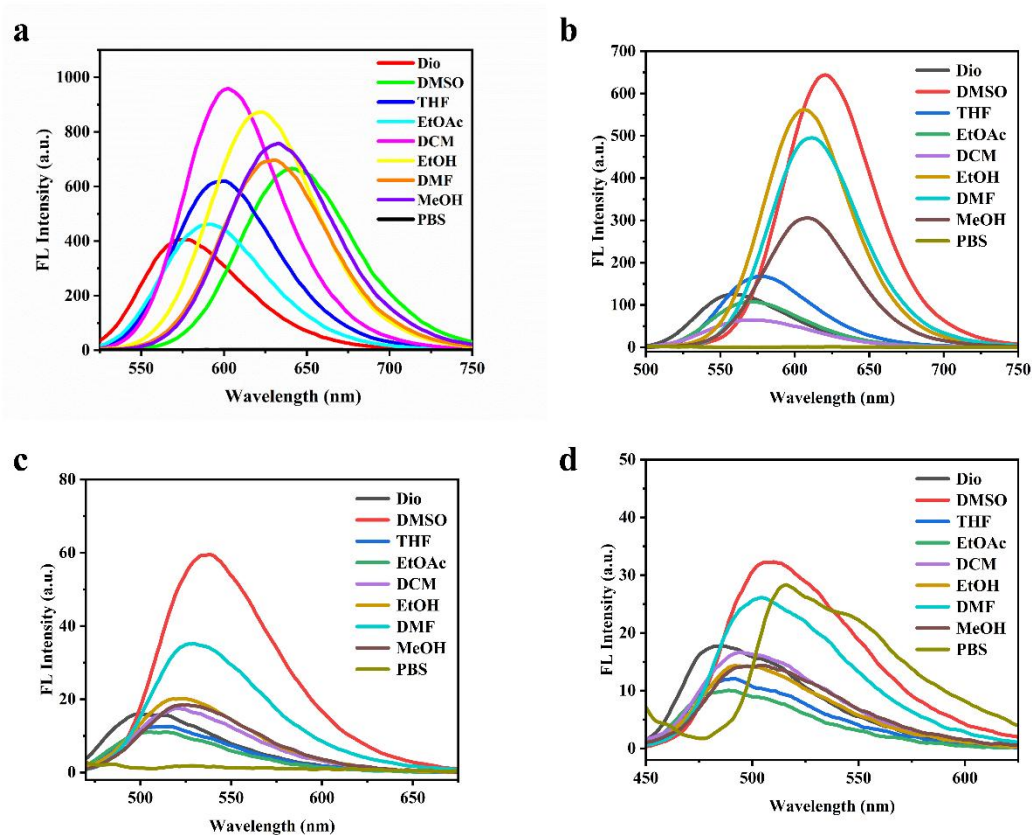


Fig 1. (a) Fluorescence emission spectra of **EDOT-EN₁** in different solvents; (b) Fluorescence emission spectra of **EDOT-EN₂** in different solvents; (c) Fluorescence emission spectra of **EDOT-EN₃** in different solvents; (d) Fluorescence emission spectra of **EDOT-EN₄** in different solvents.

As shown in Fig. S15 (a), the fluorescence intensities of **EDOT-EN₁** and **EDOT-EN₂** are similar under various water content conditions, and both are higher than those of **EDOT-EN₃** and **EDOT-EN₄** in the range of 0%–65% water content; notably, the fluorescence intensities of **EDOT-EN₁**, **EDOT-EN₂**, **EDOT-EN₃**, and **EDOT-EN₄** are

all relatively high compared with the entire test when the water content is 30%, so a water content of 30% was selected for subsequent tests. Additionally, Fig. S15 (b) presents the visual images of the four probes in EtOH solution with 30% water content, captured under daylight and UV light, respectively.

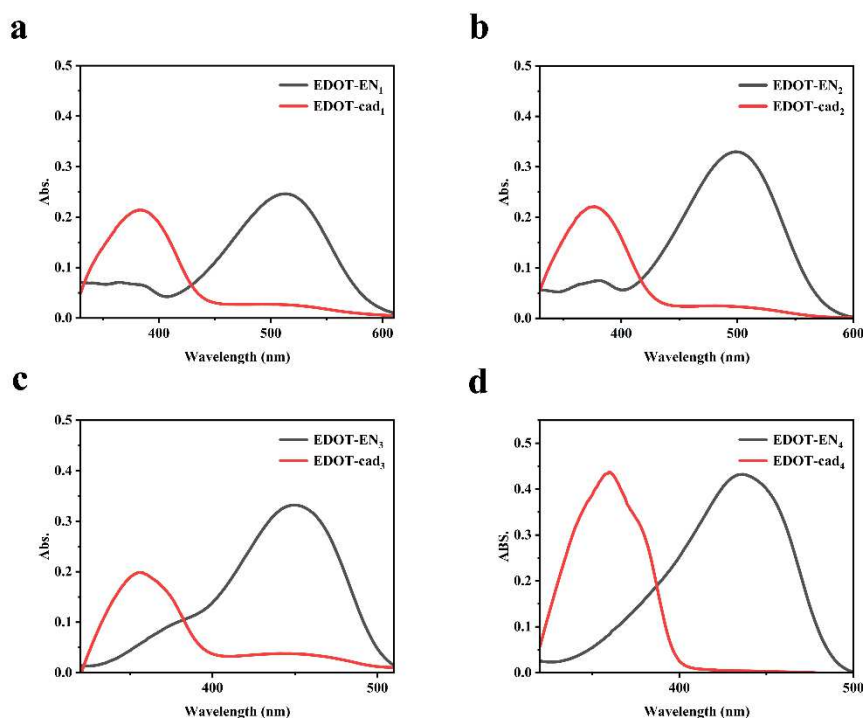


Fig 2. (a) The ultraviolet absorption spectra of **EDOT-EN₁** before and after the reaction with Cad in 30% EtOH solution; (b) The ultraviolet absorption spectra of **EDOT-EN₂** before and after the reaction with Cad in 30% EtOH solution; (c) The ultraviolet absorption spectra of **EDOT-EN₃** before and after the reaction with Cad in 30% EtOH solution; (d) The ultraviolet absorption spectra of **EDOT-EN₄** before and after the reaction with Cad in 30% EtOH solution.

As shown in Fig. 2 and Fig. 3, UV-Vis and fluorescence measurements were performed on **EDOT-EN₁**, **EDOT-EN₂**, **EDOT-EN₃**, and **EDOT-EN₄** in an environment with 30% water content before and after their reaction with Cad, respectively. The main absorption peaks of **EDOT-EN₁** and **EDOT-EN₂** are both located at approximately 520 nm, while those of **EDOT-EN₃** and **EDOT-EN₄** are slightly blue-shifted to around 450 nm; their main absorption peaks after the reaction also show a corresponding blue shift, overall presenting a gradual blue-shift trend with the weakening of the electron-donating ability of the terminal substituents. In the

fluorescence spectra, both **EDOT-EN₁** and **EDOT-EN₂** exhibit long-wavelength, high-intensity red fluorescence before the reaction, while their post-reaction product **EDOT-Cad** both show short-wavelength, moderate-intensity blue-green fluorescence; the two form a clear spectral distinction, providing an ideal signal window for selective detection. After the reaction, the fluorescence intensities of **EDOT-EN₃** and **EDOT-EN₄** decrease significantly with blue-shifted peak positions, which further confirms the regulatory effect of terminal substituents on the fluorescence properties of the probes. In addition, the fluorescence intensities of **EDOT-EN₃** and **EDOT-EN₄** are very low both before and after the reaction, and the species of **EDOT-EN₃** and **EDOT-EN₄** before and after the reaction are highly overlapping in terms of fluorescence emission peak positions and colors, resulting in insufficient signal recognition that fails to meet the requirements of selective detection; thus, no subsequent experiments were carried out.

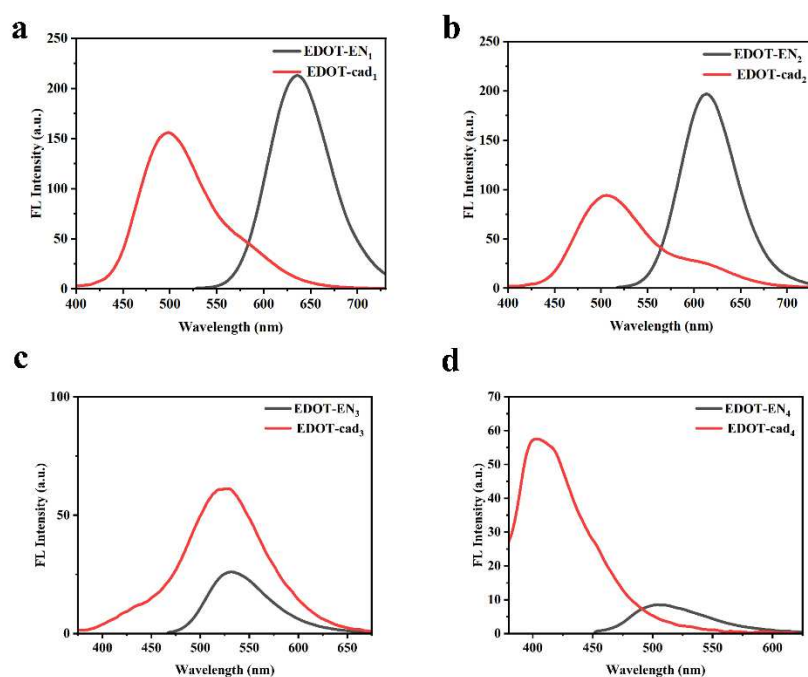


Fig 3. (a) The fluorescence emission spectra of **EDOT-EN₁** before and after reacting with Cad in 30% EtOH solution; (b) The fluorescence emission spectra of **EDOT-EN₂** before and after reacting with Cad in 30% EtOH solution; (c) The fluorescence emission spectra of **EDOT-EN₃** before and after reacting with Cad in 30% EtOH solution; (d) The fluorescence emission spectra of **EDOT-EN₄** before and after reacting with Cad in 30% EtOH solution.

As shown in Fig. 4, (a) and (b) correspond to the fluorescence spectra of the titration tests for **EDOT-EN₁** and **EDOT-EN₂**, respectively. It can be observed that **EDOT-EN₁** has a sharper, more symmetric and more stable peak shape, while the emission peak of **EDOT-EN₂** has an obvious long-wavelength shoulder peak and a broader peak shape, which is not conducive to accurate quantification and signal analysis. In addition, **EDOT-EN₁** exhibits higher response sensitivity, showing more advantages in low-concentration detection and signal quantification, and thus is a more ideal candidate probe for detection.

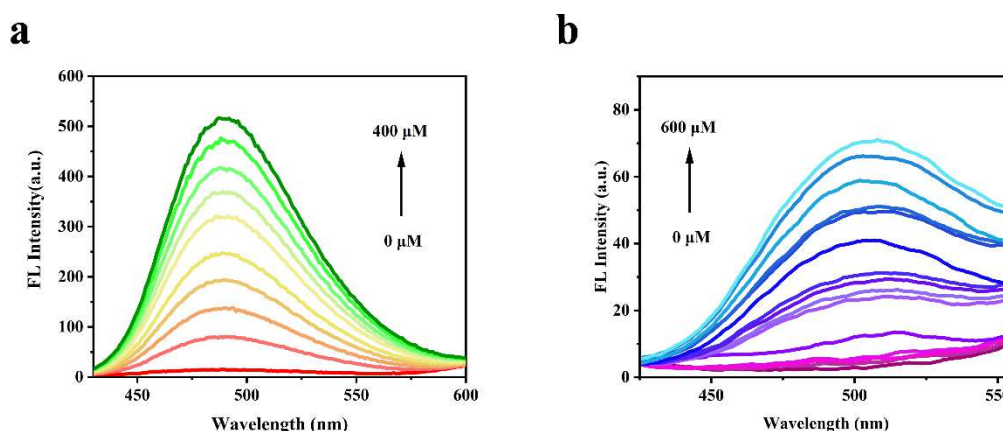


Fig 4. (a) The fluorescence emission spectra of **EDOT-EN₁** before and after reacting with Cad in 30% EtOH solution; (b) The fluorescence emission spectra of **EDOT-EN₂** before and after reacting with Cad in 30% EtOH solution.

3.2. Response study

According to the fluorescence spectra, as shown in Fig 4. (a), in the system of EtOH-PBS 7:3 (v/v), with a voltage of 550 v and a slit of 5, in the presence of **EDOT-EN₁** (10 μM), the amount of Cad (0-400 μM) is gradually increased. The fluorescence intensity gradually increases at 508 nm. Furthermore, from the linear fitting of the CAD addition amount and the fluorescence intensity at 508 nm in Fig. 5 (a), it can be seen that the intensity of the fluorescence signal has a good linear relationship with the added Cad concentration (0-400 μM), with the equation $y=35.575x+1.273$ ($R^2=0.989$). The LOD of the fluorescent probe **EDOT-EN₁** used for Cad is 0.569 μM. As shown in Fig.

5 (b), under the conditions of a voltage of 550 v and a slit of 5, the fluorescence intensity and color of the probe EDOT-EN₁ gradually change over time. The test results show that the fluorescence characteristics of the probe EDOT-EN₁ can remain stable for a long time. After adding Cad (400 μ M), the fluorescence intensity at 508 nm gradually increased, while that at 638 nm gradually decreased. The reaction is completed in approximately 50 minutes.

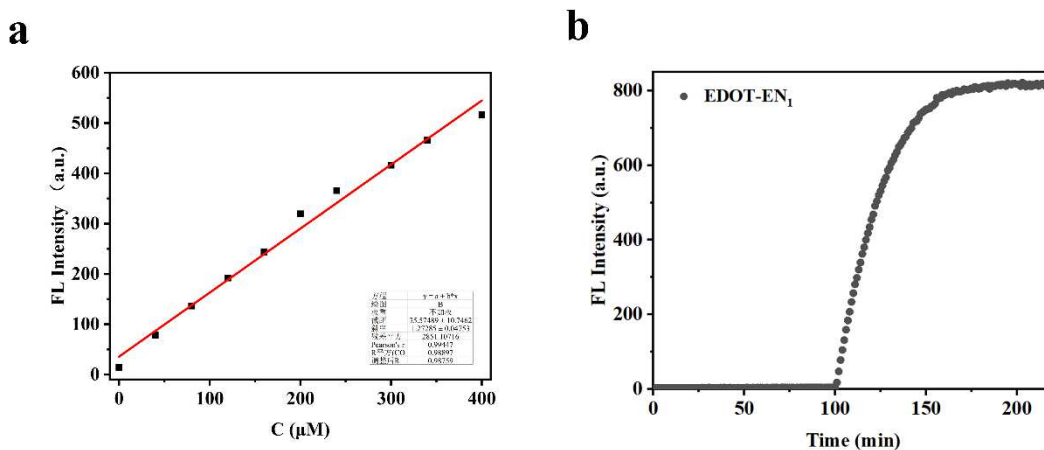


Fig 5. (a) Linear fitting of the fluorescence intensities of the responses of **EDOT-EN₁** (10 μ M) and Cad (0-400 μ M) in the EtOH-PBS (7/3, v/v) system with the addition amount of Cad. (b) Time-dependent fluorescence response measurements of the **EDOT-EN₁** probe toward Cad were performed in an EtOH-PBS (7/3, v/v) mixture with 10 μ M **EDOT-EN₁** and 400 μ M Cad.

As shown in Fig. 6a, the fluorescent probe **EDOT-EN₁** exhibits high pH tolerance and favorable fluorescence stability in the pH range of 3 to 12, which provides a feasible basis for detection under various acidic and alkaline conditions.

As shown in Fig. 6(b), fluorescence spectra were recorded in the presence of various interfering substances (400 μ M) and **EDOT-EN₁** (10 μ M) without (-) and with (+) the addition of Cad (400 μ M): 1. Blank; 2. K⁺; 3. Cu²⁺; 4. Cl⁻; 5. CO₃²⁻; 6. Ca²⁺; 7. Zn²⁺; 8. Na⁺; 9. F⁻; 10. SO₄²⁻; 11. HCO₃⁻; 12. H₂O₂; 13. Arg; 14. TBHP; 15. L - Serine; 16. Cys; 17. TEA; 18. Dip; 19. HSNO₂; 20. DEA.) The fluorescence intensity at 508 nm remained below 5 upon treatment with these interfering substances, suggesting that the probe exhibited no obvious response to them, while a remarkable enhancement in fluorescence intensity was observed upon the addition of 400 μ M Cad. These results

demonstrate that the probe **EDOT-EN₁** is barely disturbed by other competing substances during the detection of Cad and enables excellent specific recognition.

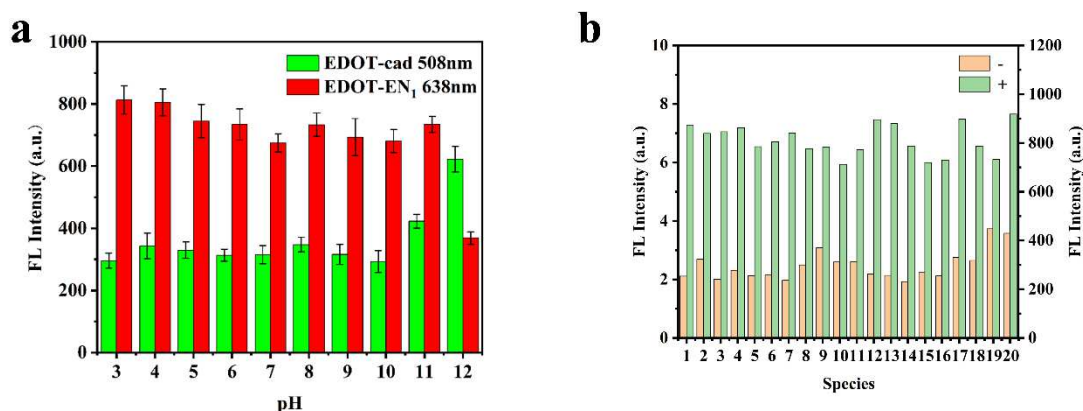


Fig 6. (a) Fluorescence intensity of **EDOT-EN₁** (10 μ M) in the EtOH-PBS (7/3) system at different pH values. Voltage: 580 v, slit: (b) Fluorescence intensities at 508 nm of **EDOT-EN₁** before and after reaction in the presence of various interfering substances. (400 μ M, 1. Blank; 2. K^+ ; 3. Cu^{2+} ; 4. Cl^- ; 5. CO_3^{2-} ; 6. Ca^{2+} ; 7. Zn^{2+} ; 8. Na^+ ; 9. F^- ; 10. SO_4^{2-} ; 11. HCO_3^- ; 12. H_2O_2 ; 13. Arg; 14. TBHP; 15. L – Serine; 16. Cys; 17. TEA; 18. Dip; 19. $HSNO_2$; 20. DEA.) Voltage: 550 v, slit: 5. (d) Fluorescence intensity at 508nm after adding Cad (10 μ M) in the presence of different interfering substances. Voltage: 580 v, slit: 5

3.3 Preparation of Probe **EDOT-EN₁** test strips and their application

Soak the filter paper (1cm²) in the **EDOT-EN₁** probe stock solution (1 mM) for 15 minutes, and then dry it in a constant temperature box at 50 °C.

As shown in Fig. 7, the prepared filter paper is cut into 1/4 cm² in size. For different solutions (400 μ M, from top to bottom and left to right, they are: 1. Blank; 2. $MgCl_2$; 3. $ZnSO_4$; 4. $CuCl_2$; 5. K_3PO_4 ; 6. H_2O_2 ; 7. $FeSO_4$; 8. $NaClO$; 9. $NaNO_2$; 10. Monoethanolamine; 11. Benzylamine; 12. Ditrdecylamine; 13. L-Arg; 14. L-Cys; 15. Hcy; 16. Furfurylamine; 17. Dimethylamine; 18. Dibutylamine; 19. Triethylamine; 20. Cad) is used for inspection. Take a drop from different solutions with a dropper and add it to the cut test paper. After reacting for two hours, observe it under the day light and the UV lamp respectively. It can be observed that all the test strips under the fluorescent lamp show a fading phenomenon. This might be due to the dilution of the probe contained on the filter paper by the added test liquid and the displacement of the probe

from its originally fixed position. However, the fading of the test strips with Cad added is more obvious. In addition, under the ultraviolet lamp, only the number 20 test paper with Cad dropped on it changed from obvious red fluorescence to white fluorescence. This indicates that the test strips prepared with the probe **EDOT-EN₁** have good selectivity and can achieve specific detection of Cad.

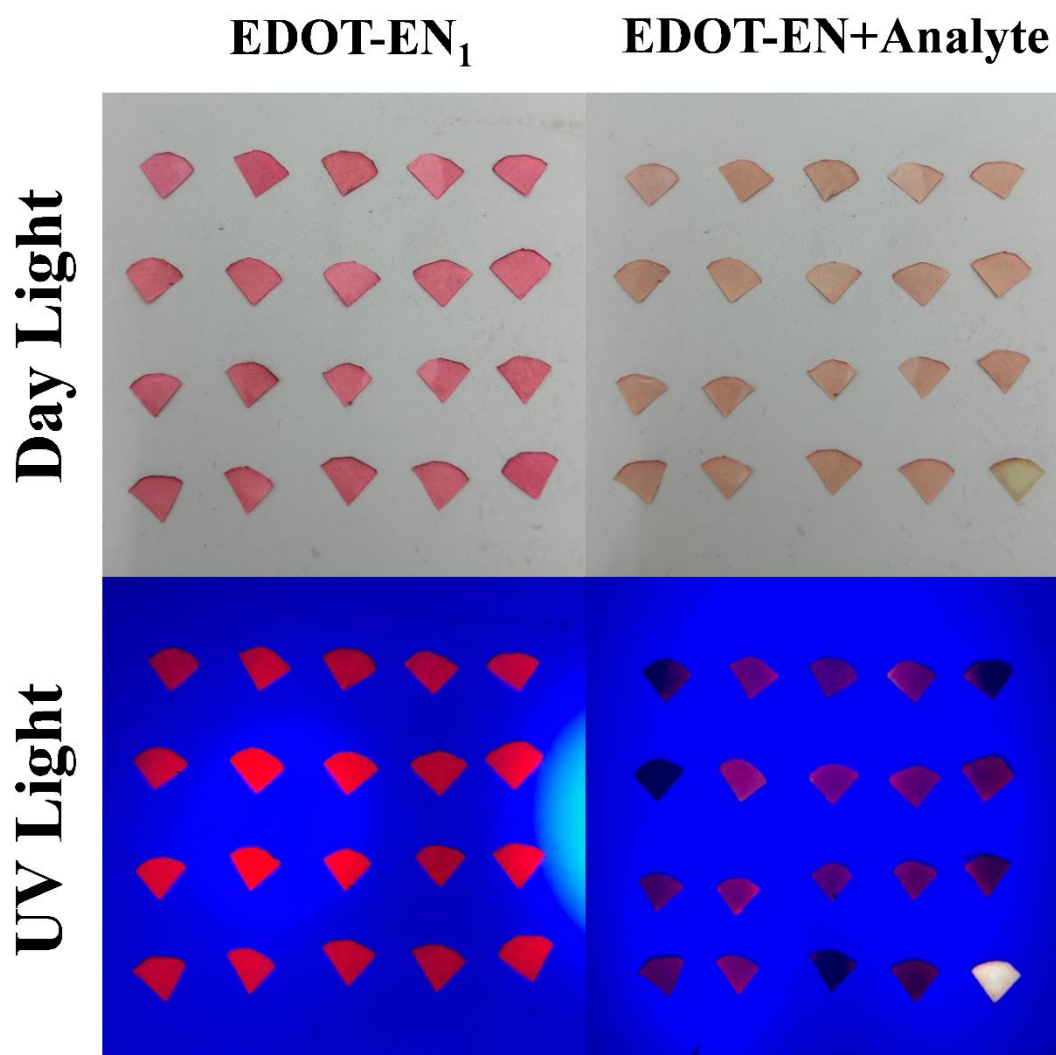


Fig 7. EDOT-EN₁ test strips (a quarter of a 1cm² circle) for the detection of different analytes, with an analyte concentration of 400 μ M, from top to bottom and left to right, they are: 1. Blank; 2. MgCl₂; 3. ZnSO₄; 4. CuCl₂; 5. K₃PO₄; 6. H₂O₂; 7. FeSO₄; 8. NaClO; 9. NaNO₂; 10. Monoethanolamine; 11. Benzylamine; 12. Ditridecylamine; 13. L-Arg; 14. L-Cys; 15. Hcy; 16. Furfurylamine; 17. Dimethylamine; 18. Dibutylamine; 19. Triethylamine; 20. Cad.

As shown in Fig. 8, divide the shrimp and fish into two groups respectively and place them in petri dishes. Put test strips in each group and moisten them with DMSO

to ensure that the test strips remain moist at all times. Then, the two samples in each group were respectively placed in a refrigerator at -8 °C and an indoor room temperature of approximately 15 °C. They were observed under fluorescent lamps and ultraviolet lamps at 0H, 3H, 10H, 1D, 2D, 3D, and 4D respectively. As shown in Fig. 4, it can be observed that as time goes by, under the fluorescent lamp, the color of the filter paper gradually fades, changing from pink to a pinkish white. The changes in the 15 °C treatment group were faster and more obvious. The changes in the -8 °C treatment group were more significant from 0 h to 3 h, and the changes were very small in the subsequent time periods. Under ultraviolet lamps, the fluorescence lightened over time. The change was more obvious in the 15 °C treatment group. For shrimp samples, the fluorescence color could be clearly observed to become dim from red at 1D, and it turned bright blue-white at 4D. The fluorescence of the fish sample group changed from red to dim at 10 h. At 3D and 4D, the fluorescence color appeared bright blue-white. In the -8 °C treatment group, the fluorescence color changes of the shrimp and fish groups were not obvious and remained red fluorescence all the time. This can reflect that with the influence of temperature and time, shrimp and fish gradually deteriorate and produce substances such as Cad. Among them, Cad can interact with **EDOT-EN₁** test strips, causing changes in the fluorescence of the test strips. Subsequently, it can be demonstrated that **EDOT-EN₁** test strips can conduct real-time detection of Cad in food samples. Especially fresh meat products rich in protein and the like.

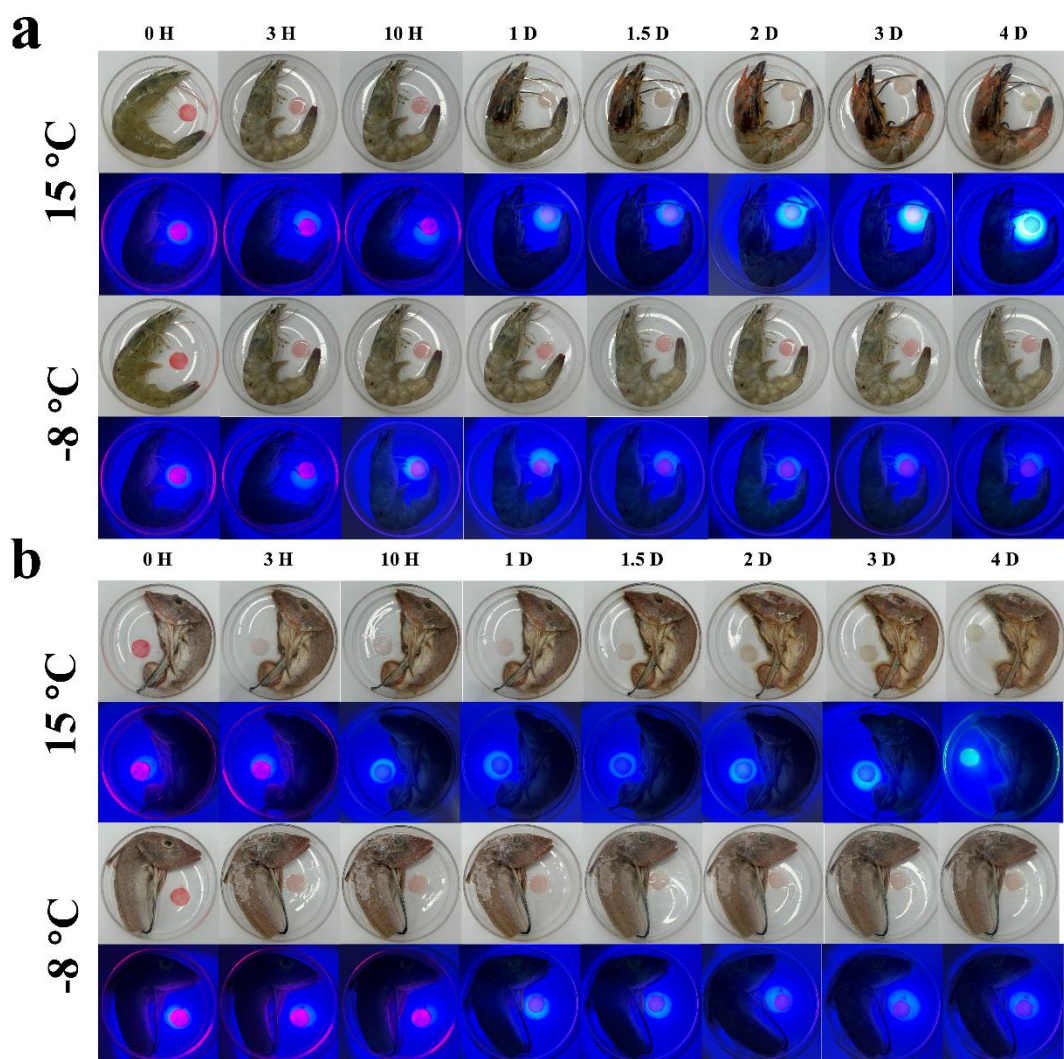


Fig 8. Shrimp and fish were each divided into two groups and placed at -8 °C and 15 °C respectively as controls. The changes of the test strips under sunlight and ultraviolet lamps for 0h,3h,10h,1D,2D,3D, and 4D were tested.

3.4 Spinning Film Test strips

In order to achieve the convenience of detecting Cad with **EDOT-EN₁** probes, we combined **EDOT-EN₁** probes with electrospinning technology to prepare **EDOT-EN₁** fluorescent probe spinning membranes. The method was to mix **EDOT-EN₁** (3.8 μg), polyurethane (HDW-3020) (2.0 g) and DMF (6.0 g) evenly and spin them using an electrospinning machine for 5 hours. As shown in Fig. 9 (a), various interfering substances (with a concentration of 400 mM) are sheared and spun on a rectangle with a size of 1 × 2 cm. 1. Blank; 2. Cad; 3. H₂O₂; 4. Diethylamine 5. Triethylamine 6. 2-

474 furfuramine; 7. 2-furanamine 8. Pyridine; 9. Trimethylamine; 10. Butylamine 11.
475 Histamine; 12. Propylamine; 13. Benzylamine 14. Arginine; 15. Cysteine; 16.
476 Glutathione 17. Na₂S; 18. NaHS. Immerse it in a water solution for 12 hours. Observe
477 under natural light and ultraviolet lamps. The research found that only in the aqueous
478 solution containing Cad, the spinning film significantly faded from red fluorescence to
479 light blue under ultraviolet lamp, which also verified the high selectivity of the spinning
480 film test paper for Cad. In addition, as shown in Fig. 9b, we suspended the spun
481 membrane test paper (1 × 2 cm) in Cad aqueous solutions of different concentrations
482 (0, 100, 200, 400 mM), and then observed it after heating it in a 45 °C water bath for
483 40 minutes. It was found that as the concentration of Cad increased. The pale red
484 fluorescence of the spinning film gradually faded. Under the treatment of Cad vapor
485 with a concentration of 400 mM, obvious fading and a faint blue fluorescence appeared,
486 verifying that the spinning film could detect Cad vapor.

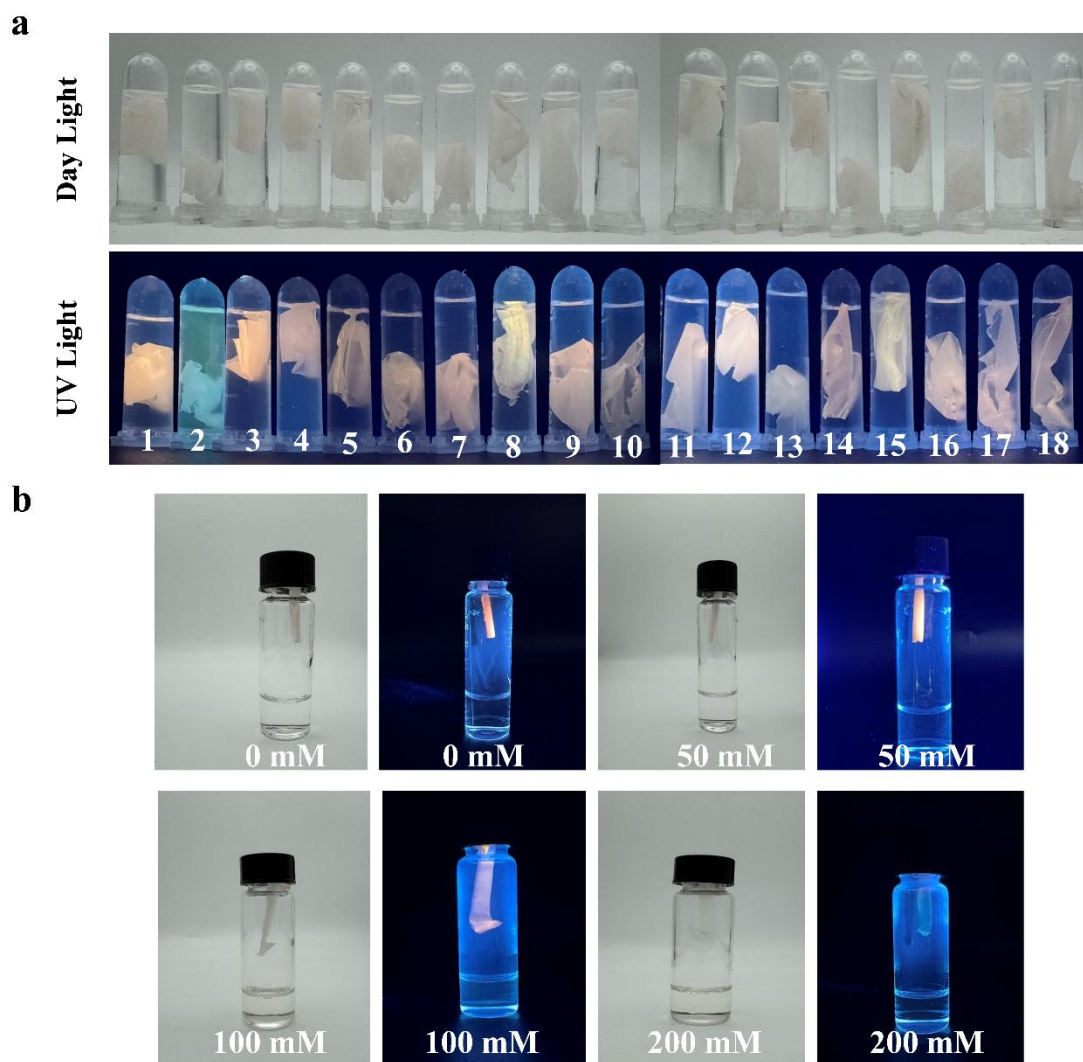


Fig 9. (a) The changes of **EDOT-EN₁** electrospun films after soaking in different analytes (400 mM) for 12 hours under sunlight and 365 nm ultraviolet light. The substances from left to right are respectively 1. Blank; 2. Cad; 3. H₂O₂; 4. Diethylamine; 5. Triethylamine; 6. 2-furfuramine; 7. 2-furanamine; 8. Pyridine; 9. Trimethylamine; 10. Butylamine; 11. Histamine; 12. Propylamine; 13. Benzylamine; 14. Arginine; 15. Cysteine; 16. Glutathione; 17. Na₂S; 18. NaHS. (b) The fluorescence intensity of the **EDOT-EN₁** electrospun membrane and the fluorescence difference of different concentrations of Cad (0,100,200,400 mM) after heating at 45 °C for 40 minutes.

3.5 Response Mechanisms

The cyano group is a common recognition group in Cad. When the probe **EDOT-EN₁** reacts with cad, EDOT-cad is generated, as shown in Fig. 10. At the same time, a small amount of EDOT-cad' will also be formed.

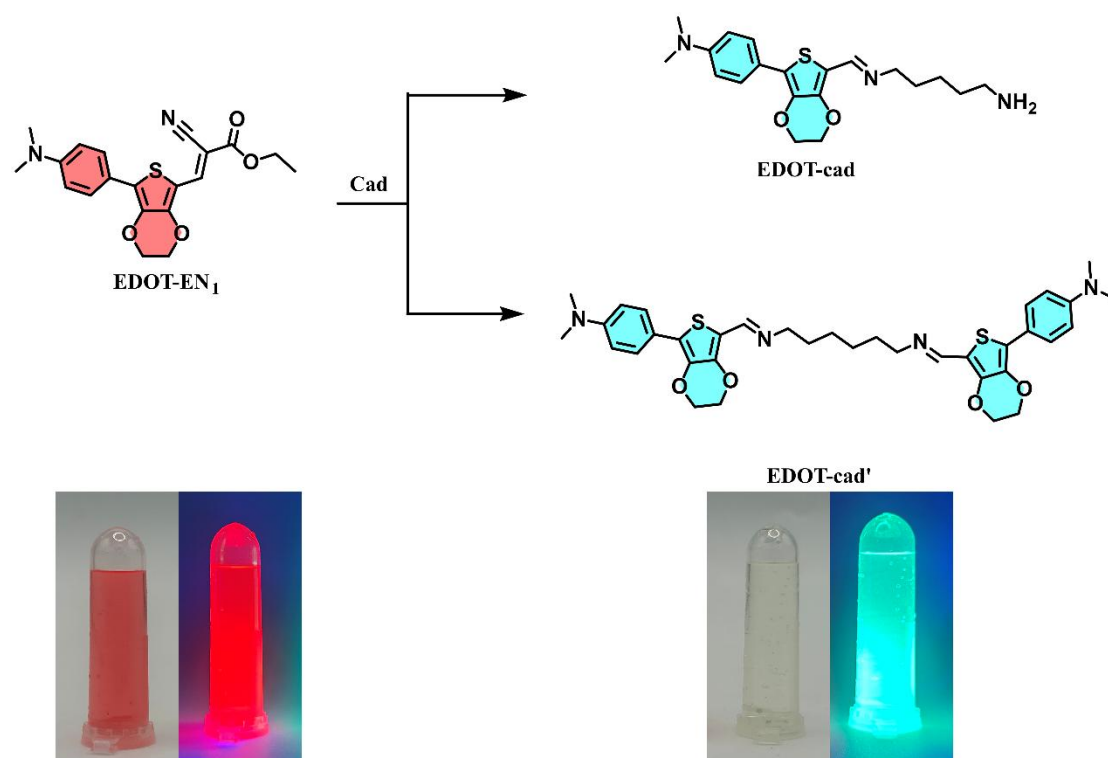


Fig 10. Schematic diagram of the response between probe **EDOT-EN₁** and Cad and the changes of the probe solution under the day light (left) and the ultraviolet lamp (right) before and after the reaction.

As shown in Fig. 11, density Functional theory (TD-DFT) analysis is underway. The figure shows the electron density distribution of the HOMO and LUMO orbitals. The HOMO electron clouds of **EDOT-EN₁** and EDOT-cad are mainly distributed in donor regions, such as electron-rich groups like N, N-dimethylamino. This indicates that in the ground state, electrons are mainly concentrated in the donor part, and the donor has the ability to provide electrons. The LUMO electron clouds of two molecules are concentrated in the receptor region, such as electron-deficient groups like cyano and ester groups. This means that the acceptor part has a tendency to accept electrons, and electrons can transition from donors to acceptors, forming an intramolecular donor-acceptor (ICT) system. The HOMO energy level of EDOT-cad is -5.82 eV, which is higher than -6.13 eV of **EDOT-EN₁**. This indicates that after the introduction of Cad, the electron cloud density in the donor part increases. The LUMO energy level of EDOT-cad is -0.30 eV, which is lower than -1.48 eV of **EDOT-EN₁**. The energy level difference ΔE of EDOT-cad is 5.52 eV, which is greater than 4.65 eV of **EDOT-EN₁**.

An increase in the energy level difference means that molecules need to absorb photons of higher energy to transition from the ground state to the excited state. According to the relationship between photon energy and wavelength, this will lead to a blue shift in the absorption spectrum. From the perspective of potential combined with the ICT effect, although an increase in energy level difference usually indicates a possible blue shift in the absorption spectrum, the simultaneous enhancement of donor and acceptor capabilities makes the ICT effect more significant.

As shown in Fig. S8, Cad titration detection was carried out on **EDOT-EN₁**. From bottom to top are the ¹H NMR data obtained after adding 0, 50, 150, and 250 μL of CAD solution (M.W. = 102.18, Purity: 98%) on the basis of 10 mg (approximately 0.026 mmol) of **EDOT-EN₁**. It can be observed that as the amount of Cad increases, the H on ethyl acetate at around 3.5 ppm gradually disappears. Meanwhile, alkyl chains characterizing Cad gradually appear at three other locations: around 2.6 ppm, 1.5 ppm, and 1.3 ppm. It can be concluded that as the addition amount of Cad increases, ethyl cyanoacetate is gradually replaced by 1, 5-diaminopentane, thereby confirming the progress site of the reaction. Meanwhile, based on the ¹H NMR of the maximum amount of Cad added, there was no peak recovery of ethyl cyanoacetate. Therefore, it can also be proved that this reaction is actually an irreversible reaction.

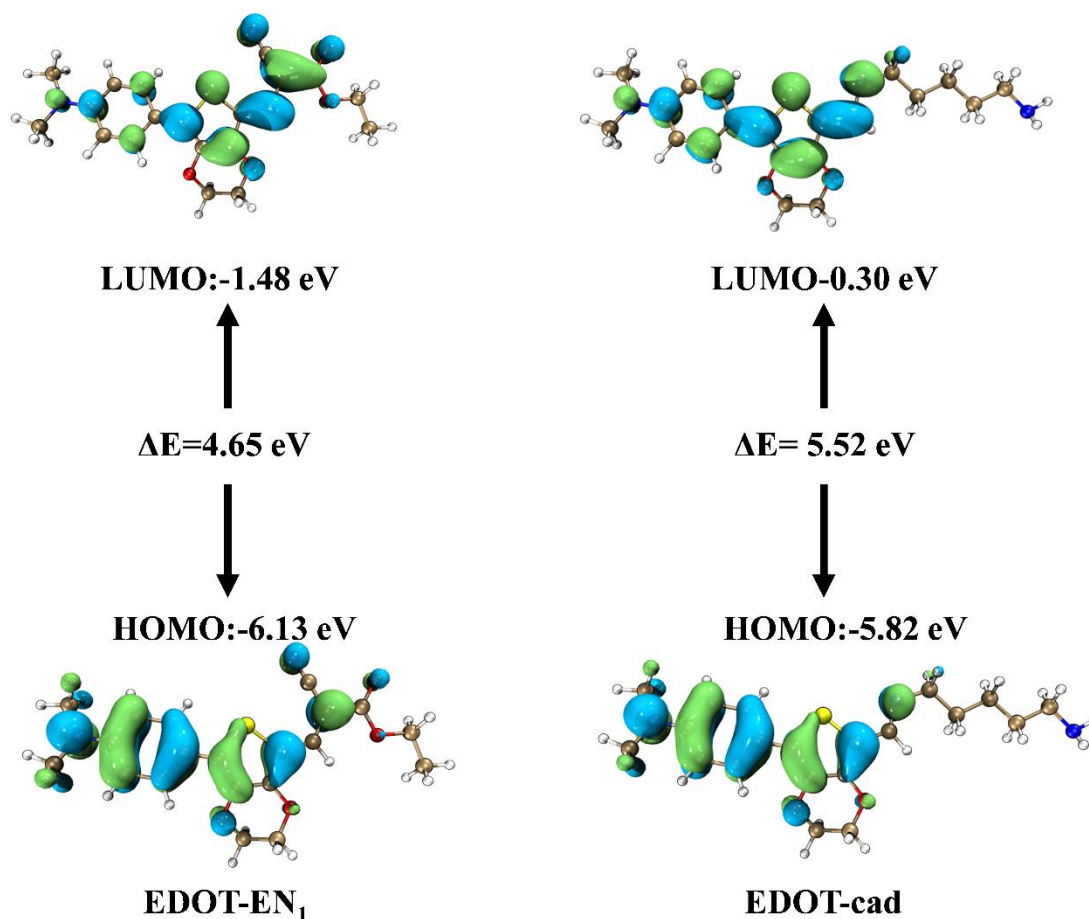


Fig 11. The frontier molecular orbitals before and after **EDOT-EN₁** response.

4. Conclusions

In summary, a fluorescent probe based on EDOT (**EDOT-EN₁**) has been successfully developed for the selective detection of Cad. This probe exhibits obvious fluorescence changes when interacting with Cad, allowing for easy visual inspection under ultraviolet illumination. The sensing mechanism involves the selective interaction of Cad and the formation of Schiff base derivatives through nitrogen-hetero-Michael addition reactions with the cyano group part. The proposed sensing mechanism was elucidated through experimental techniques (nuclear magnetic resonance, TOF-MS, UV-vis and fluorescence spectroscopy), and was supported by theoretical calculations (TD-DFT). In addition, this probe also demonstrates excellent selectivity with high sensitivity (LOD = 0.569 μM) and a fast response time ($\approx 50 \text{ min}$). Thin-film and test paper applications provide a convenient and portable sensing platform. For practical application, the electrospun film made with probes is used to detect Cad

solutions and steam, and the test strips made can achieve the detection of Cad solutions as well as the freshness of shrimp and fish. These features make it highly suitable for practical portable on-site Cad monitoring applications. These results indicate that **EDOT-EN₁** is a promising candidate probe for environmental safety analysis, providing a reliable and non-destructive method for Cad detection.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

CRedit authorship contribution statement

Guolong Su: Software, Formal analysis, Data curation, Writing-original draft.
Haitao Zhang: Conceptualization, Resources, Writing review and Editing, Supervision, Project administration. **Xin YU:** Data curation. **Xiao Chen:** Data curation. **Caixu He:** Data curation. **Xiuzhong Zhu:** Software, Supervision. **Shaoming Wang:** Software, Supervision.

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Data availability

Data will be made available on request

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