

Epirus-yellow (EY): A dual naked-eye colorimetric and NIR fluorimetric chemosensor for the rapid, sensitive, and selective detection of Sn^{2+}

Demeter Tzeli^{i,j}, Christina-Georgia Bika^a, Eirinaios I. Vrettos^a, Murugan Chinnarasu^a,
Dimitrios A. Diamantis^a, Christos Chatzigiannis^a, Zoi Kanaki^b, Uroš Javornik^c,
Nsikak B. Essien^d, Eleftherios Paraskevas Tzakos^e, Nikiforos Pertselis^f,
Despina Elizabeth Filippidou^f, Anastasios Manos^f, Janez Plavec^c, Thomas Mavromoustakos^g,
Apostolos Klinakis^b, Ramon Gonzalez-Mendez^d, George E. Kostakis^d,
Ioannis P. Gerothanassis^a, Gerasimos Malandrinos^a,
Andreas G. Tzakos^{a,h,*}

^a Department of Chemistry, University of Ioannina, Ioannina 45110, Greece

^b Center for Basic Research, Biomedical Research Foundation of the Academy of Athens, 11527, Greece

^c Slovenian NMR Centre, National Institute of Chemistry, SI-1001 Ljubljana, Slovenia

^d Department of Chemistry, School of Life Sciences, University of Sussex, Brighton BN1 9QJ, UK

^e Department of Biology, National and Kapodistrian University of Athens, Greece

^f DOTSOFT, SA, Thessaloniki, 54625, Greece

^g Department of Organic Chemistry, Faculty of Chemistry, National and Kapodistrian University of Athens, Panepistimioupoli-Zografou, 157 71 Athens, Greece

^h University Research Center of Ioannina (URCI), Institute of Materials Science and Computing, Ioannina, Greece

ⁱ Laboratory of Physical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, Athens 157 84, Greece

^j Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Ave., Athens 116 35, Greece

ARTICLE INFO

Keywords:

Sn^{2+} ion detection
NIR fluorescent probe
Turn-off chemosensor
Colorimetric detection
DFT
Canned food analysis
Smartphone chemical sensing
On-site detection
Tin toxicity

ABSTRACT

We introduce the compound (E)-2-(2-(3,4-dihydroxystyryl)-4H-chromen-4-ylidene)malononitrile, termed Epirus-Yellow (EY), as the first dual mode optical sensor for the naked-eye colorimetric and near-infrared (NIR) fluorometric selective detection of Sn^{2+} . Designed for point-of-care (POC) cellular imaging and food-safety monitoring, EY exhibits exceptional sensitivity for colorimetric (23.4×10^{-8} mol/L) and NIR fluorimetric (25.7×10^{-8} mol/L) sensing, with a near-instantaneous response and complete colorimetric transition within 400 s. 1D/2D ^{119}Sn , ^1H , and ^{13}C NMR, UV-Vis, FT-IR, thermogravimetric analysis, ICP-MS, and DFT calculations elucidated the underlying mechanism. DFT suggests EY's oxidation, forming a quinone that interacts with $\text{Sn}(\text{OH})_2$ through hydrogen bonding, leading to fluorescence. EY's applicability was demonstrated through paper strip and office scanner-assisted color quantification, with a visual detection limit of 12.0×10^{-7} mol/L. EY was successfully applied to the real-time estimation of Sn^{2+} in food and water samples, underscoring its potential for on-site food safety monitoring. Finally, a smartphone-assisted analytical platform and mobile application (Epirus4Tin) were developed, enabling user-friendly, real-time, and digital quantification of Sn^{2+} in agro-food samples.

1. Introduction

The development of rapid and selective detection methods for non-biodegradable toxic metal ions is still considered a critical challenge in the field of food chemistry. Among these metal ions, Sn^{2+} species are frequently encountered in various consumables, including canned foods,

bottled products, food-related materials, and numerous other regularly used consumer items (Meng et al., 2020). Although tin is considered an essential trace micronutrient for humans (Wang et al., 2012) and is also associated with growth factors and cancer prevention (Cheng et al., 2015), excessive intake can cause headaches, fever, skin and eye inflammation, gastrointestinal irritation, or even lead to cancer (Wang

* Corresponding author at: Department of Chemistry, University of Ioannina, Ioannina 45110, Greece.

E-mail address: atzakos@uoi.gr (A.G. Tzakos).

<https://doi.org/10.1016/j.foodchem.2026.150023>

Received 10 December 2025; Received in revised form 16 April 2026; Accepted 9 June 2026

Available online 9 June 2026

0308-8146/© 2026 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

et al., 2012). Thus, Sn^{2+} -responsive probes that can offer multifactorial responsive profiles to avoid food and water contamination are necessary. Although several optical sensors for Sn^{2+} have been reported, to our knowledge, no probe has yet combined simultaneous colorimetric and NIR fluorometric detection of Sn^{2+} .

NIR fluorimetric chemosensors are appealing due to the minimized background interference and allow measurements in colorful matrices (Ravichandiran et al., 2020). In this context, we designed and synthesized (E)-2-(2-(3,4-dihydroxystyryl)-4H-chromen-4-ylidene)malononitrile, hereafter referred to as **Epirus-Yellow (EY)** (Fig. 1), as a new chemosensing platform for tin monitoring in food-related matrices. **EY** was conceived to bridge two important gaps in the current toolkit: (i) the lack of Sn^{2+} probes that offer simultaneous naked-eye readout and near-infrared (NIR) fluorescence, and (ii) the need for fast, low-ppb, and robust detection compatible with simple, low-cost readout devices. Systematic photophysical characterization revealed that **EY** responds to Sn^{2+} with a distinct color change visible to the naked eye, alongside a marked NIR fluorescence enhancement, enabling dual-mode sensing under practical conditions. The probe displays high sensitivity in both channels, with limits of detection of 23.4×10^{-8} mol/L (colorimetric) and 25.7×10^{-8} mol/L (NIR fluorimetric), and a remarkably short response time with a complete color change within 400 s, which is particularly attractive for real-time or at-line food-safety screening. To understand the origin of this dual-mode response, we combined comprehensive spectroscopic analysis (1D/2D ^{119}Sn , ^1H and ^{13}C NMR, UV-Vis, FT-IR), thermogravimetric measurements (TGA), and inductively coupled plasma mass spectrometry (ICP-MS) with density functional theory (DFT) calculations. These studies support a mechanism in which **EY** undergoes oxidation to a quinone-like form that engages $\text{Sn}(\text{OH})_2$ through specific hydrogen-bonding interactions, triggering the observed fluorescence enhancement. Beyond solution studies, we further translated **EY** into a practical format by immobilizing it on paper test strips and quantifying the color response using a conventional office scanner. In this simple solid-state configuration, **EY** afforded a visual detection limit of 1.20×10^{-6} mol/L using an office scanner, underscoring its potential as an accessible tool for on-site assessment of Sn^{2+} contamination in food systems. **EY** is stable at room temperature for 60 days and remains intact both under elevated temperatures and UV irradiation, retaining its ability to sense tin with high selectivity, sensitivity, and rapid responsiveness. To further demonstrate its practical relevance, **EY** was successfully utilized for the detection in both water (Milli-Q, Greek mineral water, and Lake Pamvotis) and food (canned tuna and beans) samples. Finally, **EY** was integrated into a smartphone-based application that enables the real-time quantification of Sn^{2+} , offering a practical and easily accessible tool for routine food

monitoring and quality control assessments. To our knowledge, **Epirus-Yellow (EY)** represents the first chemosensing platform to successfully combine simultaneous naked-eye colorimetric and near-infrared (NIR) fluorometric detection for Sn^{2+} . Its novelty is further underscored by the development of the Epirus4Tin smartphone application, which enables rapid, on-site quantification of Sn^{2+} in food matrices without the need for expensive laboratory equipment. Ultimately, **EY**'s versatility is demonstrated by its exceptionally fast response time and dual applicability in both real-time food safety screening and live-cell NIR bio-imaging, bridging a critical gap in current Sn^{2+} monitoring technologies.

2. Experimental section

2.1. Chemistry

The materials, synthetic protocols, and spectra of **EY** are presented in the Supporting Information (Fig. S1 - Fig. S8, Table S1). **EY** is a dicyano-methylene-4H-pyran-phenol (DCPO) analog (Lu et al., 2016).

2.2. UV-vis and fluorescence spectroscopy

UV-Vis experiments were performed on an Edinburgh DS5 using a 3 mL Quartz cell. Fluorescence experiments were conducted on an Edinburgh FS5 using the same cell.

2.3. Detection limit and association constant calculation

To determine the slope of the titration curves, the absorbance at 460 nm and fluorescence intensity data at 725 nm were plotted as a function of the concentration of Sn^{2+} . The LOD was calculated using the equation $\text{LOD} = 3\sigma/k$, where σ is the standard deviation of blank measurement, and k is the slope between the absorbance value and fluorescence intensity, respectively, versus the concentration of the analyte. The association constant between Sn^{2+} and **EY** was calculated based on the changes of the fluorescence signal. A titration curve at 725 nm was plotted, and by applying linear fitting, the double reciprocal plot of the data was designed. The binding constants were derived from the Benesi-Hildebrand equation.

2.4. Colorimetric and NIR fluorimetric detection of Sn^{2+} in actual samples

The colorimetric and fluorimetric detection of Sn^{2+} was assessed using UV-Vis spectroscopy, fluorescence, and paper strips. All samples were pre-filtered to remove insoluble materials, and then different

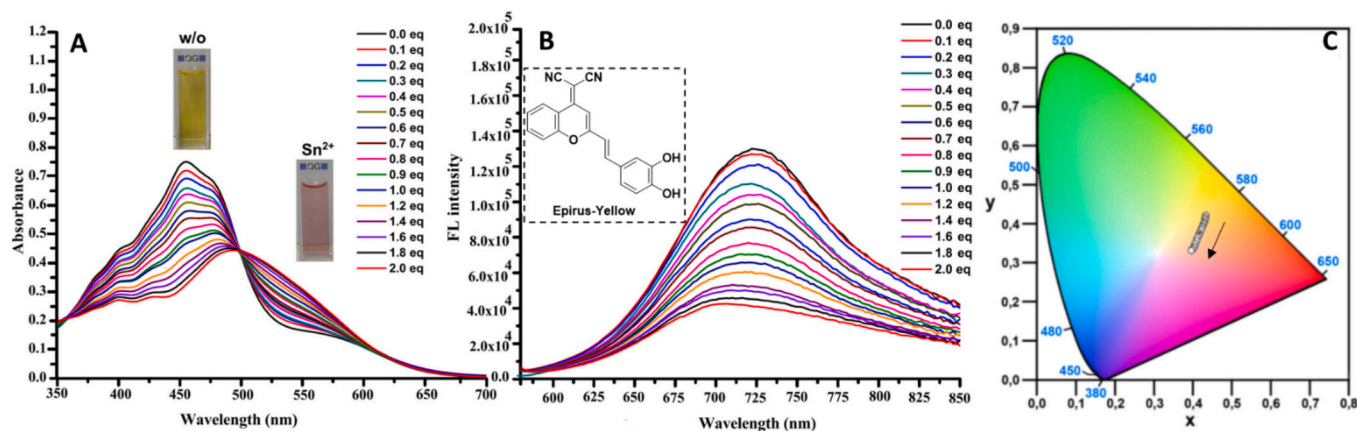


Fig. 1. Spectroscopic properties of **EY** (20 μM) in EtOH: PBS (10 mM, pH = 7.40, 2:3 v/v) upon gradual addition of different eq. of Sn^{2+} . **A)** UV-Vis spectra; **B)** Fluorescence spectra were recorded on an Edinburgh FS5 spectrophotometer; λ_{exc} = 560 nm, excitation slit = 10 nm, emission slit = 10 nm.; **C)** CIE 1931 chromaticity diagram. The structure of **EY** is illustrated as an inset in Fig. 1B.

amounts of Sn^{2+} were spiked (2.3, 4.6, 9.2 μM for UV-Vis and fluorimetry, and 0.5, 2.7, 5, and 50 μM for the paper strips). The experiments were conducted in triplicate.

2.5. Paper strips

6.56 μg of **EY** per 5.09 mg of filter paper was dissolved in methanol and added to the paper. The papers were then dried in a stream of hot air.

2.6. Paper strip stability

EY in EtOH:PBS pH = 7.4 (2:3 v/v), was added to the paper strips and was stored in a Ziploc bag at room temperature for 60 days. At specific intervals (1, 7, 15, 30, 45, and 60 days), 20 μL of a 6.6 μM Sn^{2+} solution was added, and the resulting color change was recorded using smartphone-based photography. The experiments were conducted in triplicate.

2.7. Office scanner

For the colorimetric detection of tin, an “Epson Perfection V370 Photo” scanner was used to scan the samples placed in a transparent, polystyrene, Nunc™ MicroWell™ 96-Well plate. The scans were captured as high-resolution .tif files (800 dpi, 48 bit, uncompressed).

2.8. Smartphone application

The software was developed using the Flutter Framework on Windows 10 OS. The programming language used to develop the mobile application is Dart. The mobile application was developed in the Visual Studio Code environment and tested on Android 11, Android 12, and iOS 15 devices. To ensure analytical consistency across different devices, a standardized acquisition protocol was developed within the Epirus4Tin application. Users are required to disable all automated image enhancements, including HDR, Night Mode, and AI scene detection, to prevent non-linear pixel adjustments. Images must be captured using a “Natural” color profile and 1 $\times$ optical zoom without flash. This standardization preserves raw RGB integrity and minimizes hardware-induced errors during the Euclidean distance-based quantification process.

2.9. Fluorescence cell imaging

Fluorescence cell imaging was performed in NCI-H1437 and mouse embryonic fibroblasts (MEFs) using Sn^{2+} and **EY**. Fluorescence images were captured using a fluorescence microscope (LEICA DMRA2) with 40 $\times$ magnification.

2.10. DFT calculations

EY, the corresponding quinone (**EYox**), the dimers of **EY** and **EYox** with the $\text{Sn}(\text{OH})_2$, and the complex **EYox-Sn(OH)₂** were studied via DFT calculations (B3LYP/6-31G(d,p)/LANL2DZ and B3LYP/Def2TZVP). The ethanol solvent was included implicitly via the dielectric constant solvent employing the polarizable continuum model. Harmonic frequencies were calculated to check if the optimized structures are true minima and to determine the reactions' Gibbs energies and enthalpies. The transition states were calculated by employing the STQN method. Additionally, the UV-vis absorption and emission spectra of the molecules and the dimers were calculated via the TD-DFT methodology, including the 50 lowest-energy excited singlet-spin electronic states. For the plot of the spectra, the half-width at half-height was 0.2 eV. All calculations were carried out employing the Gaussian 16 program.

2.11. Thermal and photochemical stability studies

The thermal stability of **EY** (10 μM) was evaluated in EtOH:PBS buffer (10 mM, pH 7.4, 2:3 v/v) at 37 °C and 50 °C. The integrity of the probe was monitored over time by LC-MS analysis (Fig. S9). Photochemical stability was rigorously assessed by exposing the compound to continuous UV irradiation (365 nm) for 1 h. Subsequent structural integrity and mass stability were confirmed via MS analysis (Fig. S10).

2.12. Preparation of real food samples

To validate the practical applicability of **EY**, commercially available canned food samples (beans and tuna) were analyzed. The liquid portion of each canned product was collected and centrifuged (10,000 rpm, 10 min), and the supernatant was then carefully filtered through a 0.22 μm filter to obtain a clear extract. Prior to analysis, the extracts were diluted 10-fold in EtOH/PBS (2:3 v/v). These diluted samples were then directly utilized for fluorescence measurements and subsequent standard addition (spiking) experiments.

2.13. Reversibility and competitive binding studies

To evaluate the reversibility of the **EY** probe, competitive binding experiments were performed using ethylenediaminetetraacetic acid (EDTA). Briefly, to a solution of **EY** (25 μM) in H_2O /DMSO (1:1), Sn^{2+} (25 μM) was added, and the colorimetric response was visually observed and photographed (Fig. S11). Subsequently, an aqueous solution of EDTA (50 μM) was added to the mixture, and the color recovery was monitored. This sequential addition of Sn^{2+} and EDTA was repeated for three consecutive cycles to visually assess the ON-OFF-ON switching capability and structural robustness of the probe.

3. Results and discussion

3.1. **EY** colorimetric and fluorimetric Sn^{2+} sensing ability

To evaluate the recognition ability of **EY** towards Sn^{2+} , UV-Vis and fluorescence spectroscopy titration experiments were employed (Fig. 1A). **EY** displays an absorption spectrum with λ_{max} at 460 nm and another minor band at 580 nm. Upon its exposure to an Sn^{2+} aqueous solution, two isosbestic points at 356 nm and 496 nm appear. In addition, although **EY** displays a broad fluorescence spectrum in the near-infrared (NIR) region centered at 725 nm (Fig. 1B), a change of its fluorescence signal was monitored upon the gradual addition of Sn^{2+} , accompanied by a ~ 25 nm blueshift. The exact colorimetric changes upon the gradual addition of Sn^{2+} are also depicted as points in a CIE 1931 diagram (Fig. 1C).

The detection limits were calculated to be 0.234 and 0.257 μM via UV-Vis and fluorescence spectroscopy, respectively, indicating that it is capable of detecting Sn^{2+} with high sensitivity (Fig. S13). Accordingly, the limits of quantitation (LOQ) were 0.780 μM and 0.857 μM for UV-Vis and fluorescence, respectively. Notably, the lower limit of the established linear range (2.0 μM) is higher than the LOQ, satisfying the criteria for accurate quantitation (see Fig. S13). To further evaluate the analytical standing of **EY**, a detailed comparison with previously reported Sn^{2+} chemosensors regarding detection limits, working pH, and sensing mode was performed, as summarized in Table S2. **EY** stands out for its NIR emission and dual-mode capability. The quantum yields for the probe and the complex were found to be $\Phi = 0.19$ and 0.044, respectively (Supporting Information). In addition to that, **EY** is selective towards Sn^{2+} in the presence of different metal cations, anions, and biothiols, as validated through UV-Vis and fluorescence spectroscopy (Fig. S14). Notably, **EY** readily discriminates Sn^{2+} from its oxidized Sn^{4+} counterpart (Fig. S15). Apart from Sn^{2+} , no significant responsiveness was observed, indicating that **EY** is selective towards Sn^{2+} . Time-course UV-Vis experiments revealed that **EY** responds rapidly to

Sn^{2+} , achieving full colorimetric transition in less than 400 s (Fig. S16).

Furthermore, the reversibility and structural stability of EY were evaluated, as these are critical parameters for real-world analytical applications and cost-effective screening. Competitive binding experiments were performed using EDTA. The addition of Sn^{2+} to the EY solution resulted in the expected distinct color change. However, the subsequent introduction of EDTA effectively sequestered the Sn^{2+} ions, releasing the free EY molecule and fully restoring its original color visible to the naked eye. As demonstrated in Fig. S13, this reversible ON-OFF-ON colorimetric switching was successfully maintained for multiple consecutive cycles with no apparent degradation. This visually confirms the robust structural stability of EY during the recognition process and its potential for repeated use.

3.2. Colorimetric quantification of Sn^{2+} using a simple paper strip detection assay

To offer a practical way for the detection of Sn^{2+} , a paper-strip assay was improvised. This assay utilizes standard filter papers infused with a fixed amount of EY. Solutions of decreasing concentrations of Sn^{2+} were added to the doped strips until the detection by the naked eye was considered unreliable, also known as the Visual Limit of Detection (VLOD). The resulting color change, yellow to deep orange, is illustrated in Fig. 2A. These results indicate that the developed probe can be utilized for the simple, rapid, and cost-effective detection of Sn^{2+} ions. Based on this protocol and aiming to prove its extended stability, paper strips infused with EY were prepared and stored in a Ziploc bag at room temperature. Its ability to sense Sn^{2+} was validated at certain day intervals (Fig. S14).

3.3. Colorimetric quantification of Sn^{2+} using an office scanner and a smartphone-based application

Besides the naked-eye detection of Sn^{2+} , rapid and precise methods are mandatory to distinguish color changes at low concentrations. Along these lines, a simple assay to sense Sn^{2+} via an office scanner was conceived. Solutions of EY in EtOH:PBS (10 mM, pH = 7.40, 2:3 v/v) containing increasing concentrations of Sn^{2+} were placed in a 96-well plate, which was scanned using an office scanner. The images were processed via image editing software, and the green values were extracted and plotted against the Sn^{2+} concentration (Fig. 2B). The green value decreased linearly, rendering it a quantitative assay, and the VLOD was calculated at 12×10^{-7} mol/L Sn^{2+} .

Another strategy frequently employed for the quantification of trace metals in real-life samples involves the use of smartphone-based applications (Fritz et al., 2025; Kaur et al., 2025; Ma et al., 2026; Wang et al., 2025). Accordingly, a freely available smartphone application was

developed to enable the on-demand rapid and precise quantification of Sn^{2+} levels (Fig. 2C). The relevant app, Epirus4Tin, is designed to function in a few steps. The user records or selects a picture directly from the mobile device and chooses a specific area to be analyzed. The application immediately computes and displays the detected concentration of Sn^{2+} ions. Detailed information concerning the usage of the application can be found in the supporting information.

3.4. Thermal and photochemical stability of the EY probe

To ensure the practical applicability and robustness of the EY chemosensor in real-world analytical scenarios, its thermal and photochemical stability were systematically evaluated. The thermal stability was investigated by incubating the probe at both physiological (37 °C) and elevated (50 °C) temperatures over extended periods. Chromatographic analysis (LC-MS) of the incubated samples revealed that the retention time and the integrated peak area of EY remained remarkably consistent, with no significant appearance of degradation by-products (Fig. S15). Furthermore, the photostability of the sensor was rigorously assessed by exposing the solid compound to continuous UV irradiation for 1 h. Subsequent LC-MS measurements confirmed that the probe did not undergo any photo-induced decomposition, mass loss, or photo-bleaching (Fig. S16). These findings collectively demonstrate that EY possesses exceptional thermal and photochemical stability, ensuring reliable, reproducible, and artifact-free signal readouts during its application in complex food matrices and fluctuating environmental conditions.

3.5. Detection of Sn^{2+} in standard solutions in a dual colorimetric and NIR fluorimetric mode

To further evaluate the potency of our probe in a diverse array of food chemistry-oriented applications, we tested water samples from various sources: tap, Milli-Q, Greek bottled mineral water, and Lake Pamvotis (Fig. 3A-(a)-3A-(d)). We used paper strips, fluorescence, and UV-Vis as detecting methods (Fig. S18). Sn^{2+} was not detectable in the initially tested samples; thus, the relevant samples were used as matrices for evaluating spiked Sn^{2+} concentrations. Especially Lake Pamvotis, the largest lake in Epirus, has been previously reported to lack Sn^{2+} ions (Karaouzas et al., 2021). This notion was validated using EY. To evaluate the naked-eye detection of Sn^{2+} , paper strips were used (Fig. 3A (i)), and the color changes were converted to digital signals via image processing software (Fig. 3A (ii)). After spiking increasing concentrations of Sn^{2+} , we observed again a linear response of EY via absorbance and fluorescence intensity (Fig. S18). These results confirm that EY represents an efficient sensor for Sn^{2+} in real-life samples. To evaluate the practical application of EY, real food matrices from canned beans

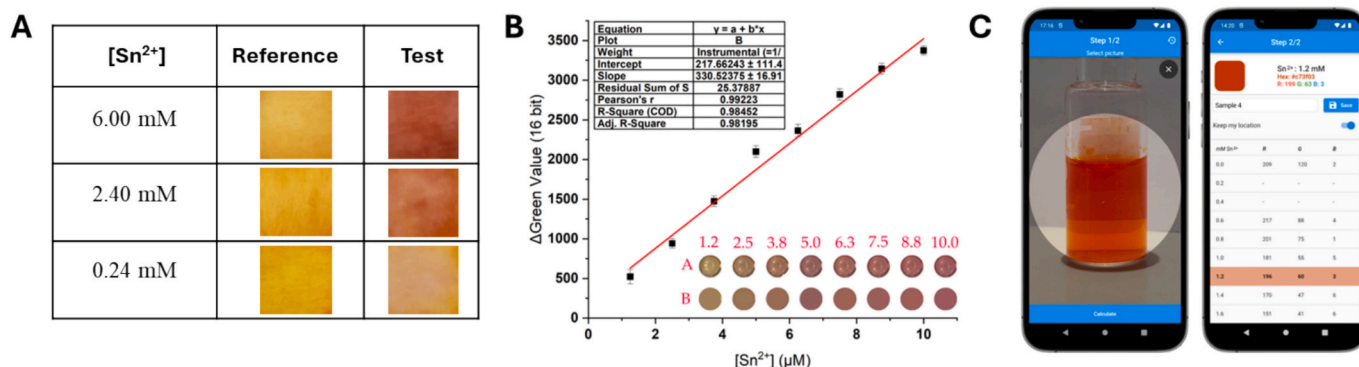


Fig. 2. A. Pictures of the litmus type assay on the added Sn^{2+} decreasing concentrations (20 μL was added each time); B. ΔGreen value (255–Green channel level) of EY as a function of $[\text{Sn}^{2+}]$. Line A: Wells as seen by the scanner. Line B: Wells homogenized by image editing software; C. The developed smartphone app for the facile and rapid measurement of Sn^{2+} levels in actual samples. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

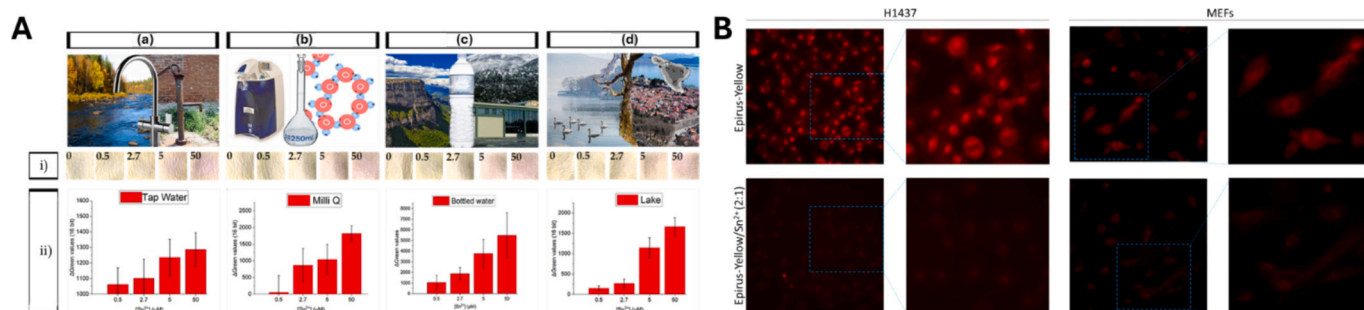


Fig. 3. A) The sensing ability of EY towards Sn^{2+} in four actual water samples: (a) Tap, (b) Milli-Q, (c) Greek bottled mineral, (d) Lake Pamvotis. In each case, the sensing ability was explored via different methods: i) Naked-eye color change using paper strips, ii) quantifying the color change from the paper strips using appropriate software. The Sn^{2+} concentration is stated for each case. B) Fluorescence microscopy image of NCI-H1437 cells and mouse embryonic fibroblasts (MEFs) treated with 12.5 μM EY or 12.5 μM EY and 6.25 μM Sn^{2+} .

and tuna were analyzed. The liquid extracts were initially diluted 10-fold to minimize potential matrix effects, and their intrinsic fluorescence was measured. Using the standard calibration curve equation ($y = -3417.0x + 132,320.7$), the native tin content was extrapolated. Factoring in the dilution, the initial Sn^{2+} concentration in the samples was successfully quantified as 96.5 μM (approx. 11.5 mg/L) for canned beans and 59.2 μM (approx. 7.0 mg/L) for canned tuna. These trace levels are fully consistent with the natural leaching from tinplate packaging and are well below the safe regulatory limit of 200 mg/L established for canned foods. Subsequently, standard addition (spiking) experiments were performed by adding a known concentration of Sn^{2+} (2.3 μM) to the diluted samples. For the canned beans extract, a quantitative recovery of approximately 128% was achieved, demonstrating the probe's reliability and accuracy in this matrix. However, for the canned tuna sample, the recovery was found to be suppressed (~25%). This behavior is highly anticipated and is attributed to strong matrix effects, specifically, the competitive chelation of Sn^{2+} by the abundant proteins, peptides, and amino acids inherently present in fish matrices, which limit the free metal available to interact with the EY probe. Despite this, the successful baseline quantification in both samples validates the immense potential of EY as a highly sensitive tool for routine food safety screening (Fig. S19). It is worth noting that the complex food matrices induced a noticeable blue shift in the emission maximum of EY (from 725 nm to ~610 nm), likely due to changes in the local micro-environment polarity or interactions with matrix biomolecules. Nevertheless, the fluorescence intensity remained linearly responsive.

3.6. Live cell NIR fluorescence bioimaging

Aiming to expand the real-life applicability of EY, its ability to sense Sn^{2+} intracellularly was studied. NIR bioimaging studies were performed in mouse MEFs and NCI-H1437 human lung tumor cells. Notably, we observed that EY shows a higher uptake in cancer cells, facilitating its rapid sensing ability (Fig. 3B). Thus, EY can be used as an Sn^{2+} bioimaging sensor. As shown in Fig. 3B, although EY is fluorescent in the NIR region in the absence of Sn^{2+} , the fluorescence ceases upon the presence of 1 eq. of Sn^{2+} . This observation validated the turn-off sensor application but simultaneously raised questions about the mode of interaction.

3.7. Control experiments to probe the EY/ Sn^{2+} sensing mechanism

To elucidate the binding mechanism, synthetic investigations were conducted in combination with various spectroscopic techniques. The interaction between EY and Sn^{2+} was analyzed using the Benesi–Hildebrand equation (Fig. S20), indicating a 3:1 stoichiometric ratio. The association constant K_a was determined graphically and calculated to be 0.21×10^5 M. Afterwards, we recorded multiple 1D and 2D NMR data to shed light on the exact interaction. Initially, a ^1H NMR titration

experiment was performed (Fig. S21A, B), revealing that the two phenolic protons of EY, resonating at 9.75 ppm and 9.18 ppm, disappeared upon addition of Sn^{2+} . To further investigate this behavior, variable temperature ^1H and ^1H – ^{13}C NMR experiments were performed in CD_3OD (Fig. S21C, S22, S23). In addition to that, 1D ^{119}Sn and 2D ^1H – ^{119}Sn HMQC NMR experiments at different temperatures were also conducted (Fig. S24–S27), and these data initially suggested that Sn^{2+} interacted with the catechol group of EY mainly via its 15-OH, as the $^4\text{J}_{\text{Sn-H14}}$ was monitored (Fig. S27), which could be considered a transient interaction.

Then, we carried out complexation reactions in 2:1, 1:1, and 1:2 M ratios (SnCl_2 :EY) in aqueous or methanolic solutions under N_2 at pH 7.4, yielding a red powder precipitate. Thermogravimetric analysis of this under N_2 revealed its instability, losing almost 17% of its weight at 325 $^\circ\text{C}$, while a slow decomposition resulted in a 0% residue at 700 $^\circ\text{C}$ (Fig. S28). The expected values for a SnO and SnO_2 as final residues regarding an SnL_2 complex are estimated at 17.5% and 19.4%, respectively (for SnL_2), while if we consider the formation of an SnL complex, then the values for the final residues are 30.3% (SnO) and 33.9% (SnO_2). Furthermore, the red product was dissolved in MeOH or DMSO and analyzed by ESI-MS (Fig. S29). In both cases, no signal corresponding to the expected complex (SnL_x) was detected; the Sn entity would be expected to exhibit its characteristic isotopic pattern. Also, ESI-MS data of the starting ligand in MeOH (Fig. S30) revealed an identical pattern. Based on these results, the formation of a complex was initially discarded. An ICP-MS experiment was then conducted to confirm the presence or absence of Sn ions by diluting the same samples used for the ESI-MS analysis, and in both cases, we observed the characteristic isotopic pattern of Sn species (Fig. S31). The latter result indicates the minimal presence of Sn in the red solid. Taking these studies into consideration, along with the NMR and IR (Fig. S32) data of the ligand and red solid, we considered that the red precipitate corresponded to the oxidized version of the organic ligand (Scheme S2). However, the following notions should be considered: 1) Solution studies of SnCl_2 in aqueous or protic media suggest that at physiological pH values, Sn exists in the form of an $\text{Sn}(\text{OH})_2$ species (Cigala et al., 2012; Séby et al., 2001) (Scheme S3). This hypothesis excludes the formation of polynuclear species and is valid for precise concentrations (10^{-7} mol/L), similar to the observed experimental data. 2) At pH 7.4, the $\text{Sn}(\text{OH})_2$ species has a very characteristic geometry (Persson et al., 2016). The lone pair of the Sn entity induces a trigonal geometry; thus, the two hydroxyl groups are almost perpendicular. On this occasion, the two OH entities sit weakly in a perfect arrangement to interact (Scheme S2) Given that a) the redox potentials for Sn are $E_0 = 0.27$ V for ($\text{Sn}^{4+}/\text{Sn}^{2+}$) and $E_0 = -0.14$ V for ($\text{Sn}^{2+}/\text{Sn}_0$) (Bajnóczi et al., 2014; Piskunov et al., 2019) and for a typical catechol is 0.795 V for two electrons (Robole et al., 2019), b) EY is a radical-based ligand which can be oxidized when exposed in the open air (Devonport et al., 2021; Piskunov et al., 2019), c) a redox non-innocent solvent was utilized (MeOH) (Andrew

et al., 1976), d) the impact and presence of atmospheric O_2 cannot be ignored, e) the redox catalytic efficacy of $SnCl_2 \cdot 2H_2O$ at room temperature in the presence of protic components (Menezes et al., 2013) we can conclude that the received final red compound corresponds to the oxidized quinone (Scheme S2). This process is triggered by the peculiar geometry of the $Sn(OH)_2$ species and the presence of a redox non-innocent environment (MeOH or O_2). The peculiar geometry of the $Sn(OH)_2$ entity can explain the observed selectivity over other cations.

Aiming to examine the hypothesis that EY undergoes oxidation followed by complexation with Sn ions, DFT calculations were employed. The minimized structures of all the compounds implicated in the proposed mechanism were first computed, and the enthalpy change associated with each step of the mechanism was determined. Finally, the theoretical IR, UV-Vis, and emission spectra were generated and compared with the experimental data to validate our hypothesis and elucidate the precise complexation mechanism.

3.8. DFT calculations: Structures and reaction mechanism

The calculated minima i.e., EY, quinone (EYox), dimers of EY and EYox with the $Sn(OH)_2$, i.e., tEY... $Sn(OH)_2$ and tEYox... $Sn(OH)_2$, the complex EYox- $Sn(OH)_2$, and transition structures involved in the processes involved in the detector are given in Fig. 4 and Fig. S35-S36. The interaction in dimers is denoted as "...", while the complexation between EY or EYox with $Sn(OH)_2$ is denoted as "-". The tEYox- $Sn(OH)_2$ complex has single C—O bonds with C—O distances of about 1.37 Å. tEYox is reduced, i.e., two e^- have been transferred from the Sn(II) to EYox, while the Sn atom has been oxidized to Sn(IV). As a result, the Sn—O bond distances of the $Sn(OH)_2$ have become shorter by about 0.5 Å (Fig. 4). The reaction formation of complex 6 either starts from 7 or 5 via 9 (Fig. 5 and Fig. S36). The reaction paths for the formation of 5 and 6 are depicted in Fig. 5 and Fig. S37 & S38. Reaction Gibbs energies and

enthalpies are given in Table S3. 1 (tEY) forms hydrogen bonds with $Sn(OH)_2$ via its isomer 2 with a binding enthalpy of -3.9 kcal/mol. The main absorption peaks of 1 correspond to the energy demand for the homolytic cleavage of one O—H of 1 (Fig. 5), where the absorption band energy is plotted. Thus, the homolytic cleavage of one O—H bond is mediated by the absorption energy, and then the second one is covered by that absorbed energy. Quinone 3 forms two hydrogen bonds with the $Sn(OH)_2$ molecule with a reaction enthalpy of -3.6 kcal/mol. 5 can lead to the formation of 6 via the reaction path, which is depicted in Fig. 5. While the reaction energy demands for the formation of 6 are about 6 kcal/mol, there is a solvent network of ethanol that needs to be broken to rotate the OH groups of $Sn(OH)_2$. Then, the Sn atoms are coordinated with the O atoms of the quinone via a redox reaction, where the quinone is reduced, and the Sn is oxidized (from II to IV oxidation state). The ethanol-ethanol binding energy is -5.6 kcal/mol (Ghoufi et al., 2016), while for small ethanol clusters of six molecules, the binding energy is -55.6 kcal/mol (Malloum et al., 2020). Thus, while the reaction energy path for the formation of 6 from 5 is small, the ethanol network slows down the reaction.

3.9. Calculated IR spectra

The calculated IR spectra of tEY, tEYox, dimers of tEY and tEYox with $Sn(OH)_2$, complex tEYox- $Sn(OH)_2$, and the free $Sn(OH)_2$ have been plotted in Fig. 6 and Fig. S39-S40. As shown, there are many IR peaks in the region 1200 – 2000 cm^{-1} . Note that there is one very strong peak that corresponds to a vibrational stretching normal mode of the whole tEY or tEYox, except for the two CN groups, which remain rigid. In all cases, i.e., tEY, tEYox, the dimers of tEY and tEYox with the $Sn(OH)_2$, this peak is at ~ 1630 cm^{-1} except for the complex tEYox- $Sn(OH)_2$, where this peak is at 1506 cm^{-1} , at our best methodology (B3LYP/Def2TZVP method), as shown in Fig. 6. Thus, only the complexation results in this red shift of

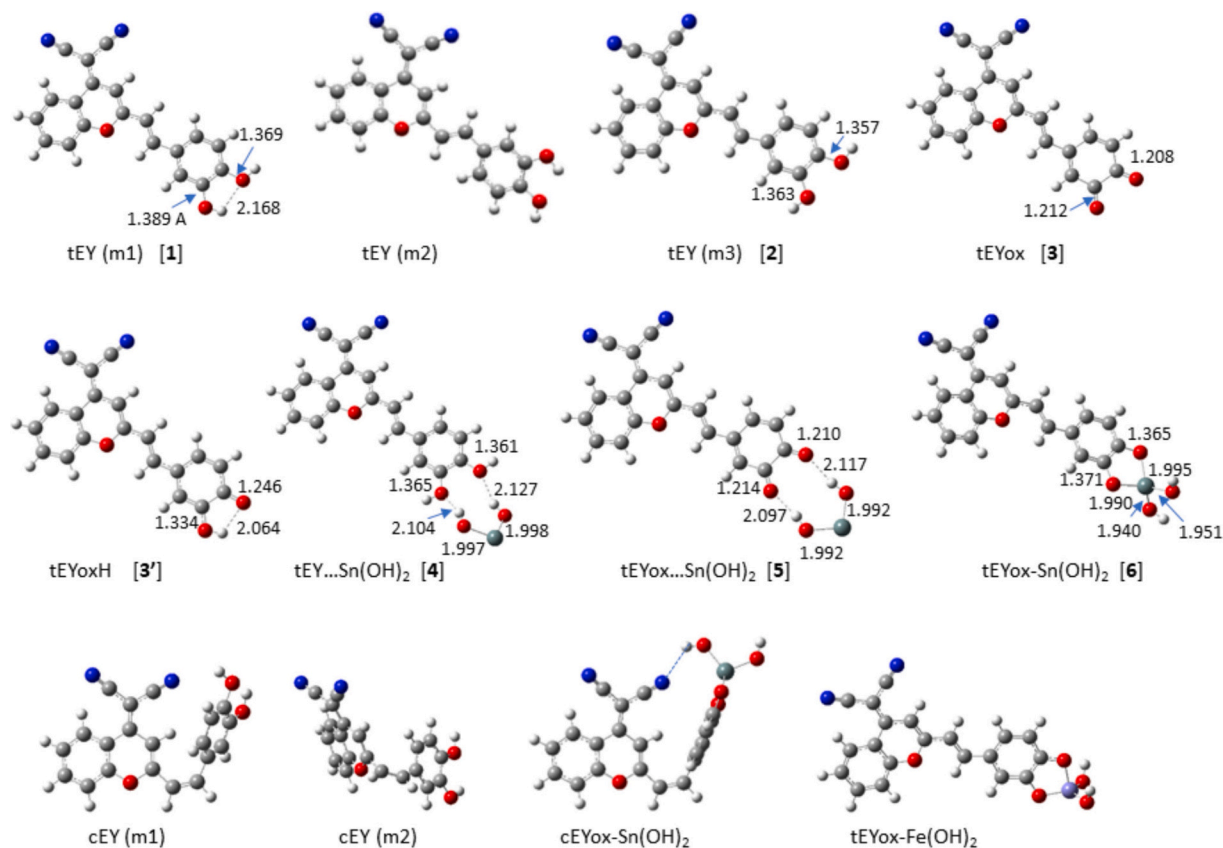


Fig. 4. Calculated minimized structures of EY, quinone (EYox), and their dimers with $Sn(OH)_2$. The interaction in dimers is denoted as "...", and between EY or EYox and $Sn(OH)_2$ as "-". The distances of the C—O and Sn—O bonds are depicted.

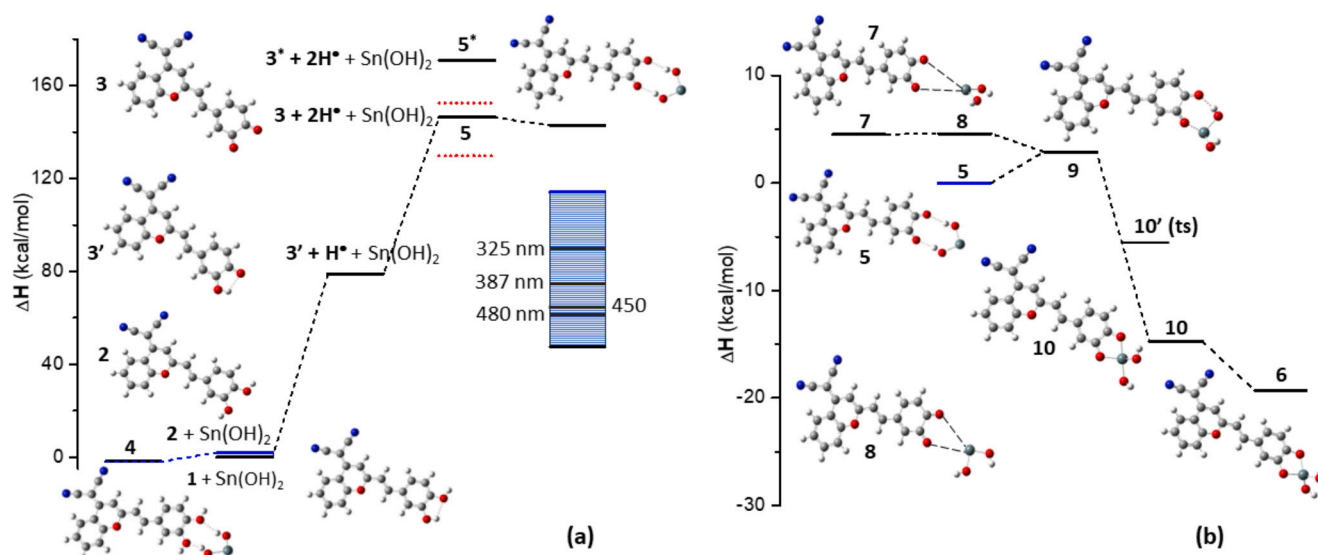


Fig. 5. Reaction enthalpies paths of the (a) formation of 5, red dot lines correspond to reaction Gibbs energies; (b) Formation of 6 at the B3LYP/def2tzvp. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

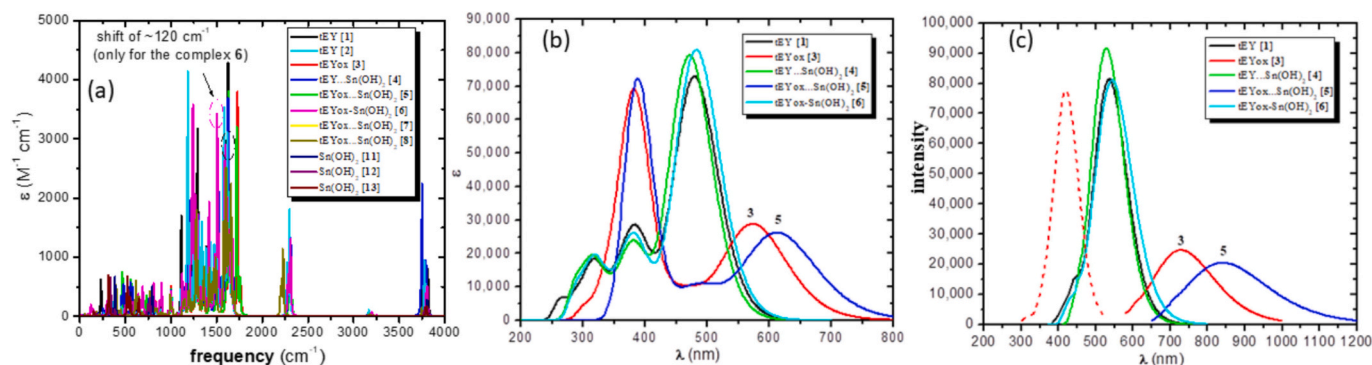


Fig. 6. (a) IR, (b) absorption, and (c) fluorescence spectra (dot line corresponds to $S_2 \rightarrow S_0$ deexcitation) of the calculated minimum structures of EY, EYox, their dimers with $\text{Sn}(\text{OH})_2$, and the corresponding complex.

about 120 cm^{-1} (Fig. S39–S40). Experimentally, also no shift was observed (Fig. S32), showing that the complex has not been formed.

3.10. Calculated UV–Vis absorption and emission spectra

Computationally, the first main Vis absorption peak of 1 (tEY) and 4 (tEY... $\text{Sn}(\text{OH})_2$) is calculated around 450 nm, i.e., 420 nm–480 nm, depending on the methodology and the molecular system. Specifically, the absorption peak of the dimer is blue-shifted up to 8 nm. These calculated values are in excellent agreement with the experimental value of 450 nm, showing that initially in the detector, there is tEY. On the contrary, quinone 3 (tEYox) has an absorption peak at 574 nm, while its dimer with $\text{Sn}(\text{OH})_2$ is significantly red-shifted at 613 nm. The main Vis absorption peak of the complex tEYox- $\text{Sn}(\text{OH})_2$ is at 483 nm, see Fig. 6, Table S4, and Fig. S41–S42.

The experimental fluorescence spectrum shows a main fluorescent peak at 725 nm. Comparing the calculated spectra with the experimental one, it seems that the emission spectra correspond to the quinone 3 (tEYox) and to 5 (tEYox... $\text{Sn}(\text{OH})_2$), which present fluorescent peaks at 729 and 840 nm. On the contrary, 1, 4, and 6 present fluorescent peaks that range from 529 nm to 544 nm, see Fig. 6 and Fig. S43.

The frontier molecular orbitals (Fig. S45) involved in the main absorption ($\text{H} \rightarrow \text{L}$ and $\text{H}-1 \rightarrow \text{L}$) and fluorescence ($\text{H} \rightarrow \text{L}$ and $\text{H}-1 \rightarrow \text{L}$) peaks are similar because the electron charge is in the EY or EYox

molecules. However, in the case of the tEYox... $\text{Sn}(\text{OH})_2$ the absorption peak at 500 nm is a charge transfer excitation from the $\text{Sn}(\text{OH})_2$ to tEYox.

Thus, DFT calculations show that in the processes involved in the detector, the dimers of the oxidized quinone (EYox) with $\text{Sn}(\text{OH})_2$ are involved, while the complex of EY with the $\text{Sn}(\text{OH})_2$ is not formed. Specifically, EY is oxidized via the UV–vis absorption process, and the quinone interacts with $\text{Sn}(\text{OH})_2$ via hydrogen bonds. This dimer fluoresces, while the complex of EY with the $\text{Sn}(\text{OH})_2$, where the $\text{Sn}(\text{IV})$ is involved, is not formed.

4. Conclusions

This work reports the synthesis of EY, the first dual-mode optical probe for Sn^{2+} , enabling Near-Infrared fluorimetric sensing (emission at 725 nm) alongside naked-eye colorimetric recognition. Notably, EY's sensing response to Sn^{2+} is almost instantaneous, achieving the complete colorimetric change within 400 s, and is highly selective towards Sn^{2+} over other competing ions. EY is stable at room temperature even after 60 days, while also staying intact under elevated temperature and photo irradiation. The colorimetric detection capability of EY was exploited for the development of a practical paper strip assay and a simple office scanner-assisted color quantification assay. Additionally, its color-changing response was successfully integrated into a developed

and freely available smartphone application to enable rapid, user-friendly, real-time Sn^{2+} measurements. The colorimetric and fluorimetric detection of Sn^{2+} was validated in six real-world matrices (four water and two food samples), confirming its applicability for routine analysis. EY can effectively detect Sn^{2+} at concentrations of 23.4×10^{-8} and 25.7×10^{-8} mol/L via UV-Vis and fluorescence spectroscopy, respectively, while the visual limit of detection for the paper strips and the office scanner was determined to be 50.0×10^{-7} mol/L and 12.0×10^{-7} mol/L, respectively. Comprehensive mechanistic studies supported by DFT calculations revealed that EY undergoes oxidation through the UV-Vis absorption process, forming a quinone species that interacts with $\text{Sn}(\text{OH})_2$ via hydrogen bonding. This hydrogen-bonded dimer fluoresces, whereas the formation of a coordination complex between EY and $\text{Sn}(\text{OH})_2$ involving $\text{Sn}(\text{IV})$ does not occur, since the ethanol network slows down the reaction. EY can thus be efficiently employed as a practical and robust chemosensor for the selective and rapid detection of Sn^{2+} , rendering it an appealing probe for food monitoring and routine industrial applications.

CRedit authorship contribution statement

Demeter Tzeli: Visualization, Investigation, Writing – review & editing, Formal analysis. **Christina-Georgia Bika:** Investigation, Visualization, Writing – review & editing. **Eirinaios I. Vrettos:** Writing – review & editing, Writing – original draft, Visualization, Investigation. **Murugan Chinnarasu:** Investigation, Visualization, Writing – review & editing. **Dimitrios A. Diamantis:** Writing – original draft, Visualization, Investigation. **Christos Chatzigiannis:** Investigation. **Zoi Kanaki:** Visualization, Investigation. **Uroš Javornik:** Visualization, Investigation. **Nsikak B. Essien:** Investigation. **Eleftherios Paraskevas Tzakos:** Writing – review & editing. **Nikiforos Pertselis:** Software. **Despina Elizabeth Filippidou:** Software. **Anastasios Manos:** Software. **Janez Plavec:** Investigation. **Thomas Mavromoustakos:** Writing – review & editing, Supervision. **Apostolos Klinakis:** Writing – review & editing, Supervision, Resources. **Ramon Gonzalez-Mendez:** Investigation. **George E. Kostakis:** Writing – review & editing, Supervision, Investigation. **Ioannis P. Gerothanassis:** Writing – review & editing. **Gerassimos Malandrinos:** Writing – review & editing, Supervision. **Andreas G. Tzakos:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The research work was supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the “First Call for H.F.R.I. Research Project to support Faculty members and Researchers and the procurement of high-cost research equipment grant” (Project Number: 991). This work was further supported by the project BIOCHAIN – Strengthening Biodiversity Preservation through Sustainable Exploitation of the Bioresources Chain in the Programme Area (Project ID: 6006563), co-funded by the European Union and the National Funds of the Countries participating in the Interreg VI-A Greece–Italy 2021–2027 Programme.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodchem.2026.150023>.

[org/10.1016/j.foodchem.2026.150023](https://doi.org/10.1016/j.foodchem.2026.150023).

Data availability

No data was used for the research described in the article.

References

- Andrew, M. R., Drury, J. S., McNicol, B. D., Pinnington, C., & Short, R. T. (1976). The characterization of Pt/Sn catalyst for the electrochemical oxidation of methanol. *Journal of Applied Electrochemistry*, 6(2), 99–106.
- Bajnóczi, É. G., Czeglédi, E., Kuzmann, E., Homonnay, Z., Bálint, S., Dombi, G., ... Persson, I. (2014). Speciation and structure of tin(II) in hyper-alkaline aqueous solution. *Dalton Transactions*, 43(48), 17971–17979.
- Cheng, J., Yang, E., Ding, P., Tang, J., Zhang, D., Zhao, Y., & Ye, Y. (2015). Two rhodamine based chemosensors for Sn^{4+} and the application in living cells. *Sensors and Actuators B: Chemical*, 221, 688–693.
- Cigala, R. M., Crea, F., De Stefano, C., Lando, G., Milea, D., & Sammartano, S. (2012). The inorganic speciation of tin(II) in aqueous solution. *Geochimica et Cosmochimica Acta*, 87, 1–20.
- Devonport, J., Sully, L., Boudalis, A. K., Hassell-Hart, S., Leech, M. C., Lam, K., ... Kostakis, G. E. (2021). Room-Temperature Cu(II) Radical-Triggered Alkyne C–H Activation. *JACS Au*, 1(11), 1937–1948.
- Fritz, A. P., Schubert, J., Stopper, P., Diekemper, D., Huhn, C., & Schwarzer, S. (2025). Chemistry meets environmental science: A simple colorimetric assay for glyphosate detection in school laboratories. *Journal of Chemical Education*, 102, 8, 3592–3599.
- Ghoufi, A., Artzner, F., & Malfreyt, P. (2016). Physical properties and hydrogen-bonding network of water–ethanol mixtures from molecular dynamics simulations. *The Journal of Physical Chemistry, B*, 120, 793–802.
- Karaouzas, I., Kapetanaki, N., Mentzafou, A., Kanellopoulos, T. D., & Skoulidakis, N. (2021). Heavy metal contamination status in Greek surface waters: A review with application and evaluation of pollution indices. *Chemosphere*, 263, Article 128192.
- Kaur, M., Virender, V., Singh, J., Kumar, A., & Dubey, S. K. (2025). Smartphone-based analytical platform for real-time, reversible detection of Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} ions. *Food Chemistry*, 492(2), Article 145388.
- Lu, Z., Wu, J., Liu, W., Zhang, G., & Wang, P. (2016). A ratiometric fluorescent probe for quantification of alkaline phosphatase in living cells. *RSC Advances*, 6(38), 32046–32051.
- Ma, H., Li, Y., Zhang, X., Yan, L., Gao, H., Liu, L., & Xu, L. (2026). A phenothiazine-based fluorescent probe for ultrafast and selective hypochlorous acid detection with hydrogel-integrated smartphone readout. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 348(1), Article 127114.
- Malloum, A., Fife, J. J., & Conradie, J. (2020). Exploration of the potential energy surfaces of small ethanol clusters. *Physical Chemistry Chemical Physics*, 22, 13201–13213.
- Menezes, F. D. L., Guimaraes, M. D. O., & da Silva, M. J. (2013). Highly selective SnCl_2 -catalyzed Solketal synthesis at room temperature. *Industrial & Engineering Chemistry Research*, 52(47), 16709–16713.
- Meng, X., You, L., Li, S., Sun, Q., Luo, X., He, H., Wang, J., & Zhao, F. (2020). An ICT-based fluorescence enhancement probe for detection of Sn^{2+} in cancer cells. *RSC Advances*, 10(62), 37735–37742.
- Persson, I., D'Angelo, P., & Lundberg, D. (2016). Hydrated and solvated tin(II) ions in solution and the solid state, and a coordination chemistry overview of the d10s2 metal ions. *Chemistry – A European Journal*, 22(51), 18583–18592.
- Piskunov, A. V., Tsys, K. V., Cherev, M. G., & Cherkasov, A. V. (2019). Tin(II) Complexes Based on N-Alkyl-Substituted o-Amidophenolate Ligands: Acid–Base and Redox Transformations. *Russian Journal of Coordination Chemistry*, 45(9), 626–636.
- Ravichandiran, P., Prabakaran, D. S., Bella, A. P., Boguszewska-Czubara, A., Maslyk, M., Dineshkumar, K., ... Yoo, D. J. (2020). Naphthoquinone-dopamine linked colorimetric and fluorescence Chemosensor for selective detection of Sn^{2+} ion in aqueous medium and its bio-imaging applications. *ACS Sustainable Chemistry & Engineering*, 8(29), 10947–10958.
- Robole, Z. M., Rahn, K. L., Lampkin, B. J., Anand, R. K., & VanVeller, B. (2019). Tuning the electrochemical redox potentials of catechol with boronic acid derivatives. *The Journal of Organic Chemistry*, 84(4), 2346–2350.
- Séby, F., Potin-Gautier, M., Giffaut, E., & Donard, O. F. X. (2001). A critical review of thermodynamic data for inorganic tin species. *Geochimica et Cosmochimica Acta*, 65(18), 3041–3053.
- Wang, P., Li, S., Pu, C., Cao, X., Jia, M., Ai, J., Yue, Y., Biquem, R., & An, Y. (2025). Highly selective and sensitive colorimetric and fluorescence detection of copper(II) and glyphosate using dual-functional peptide probe and its multifarious applications in food sample analysis and bioimaging. *Food Chemistry*, 491, Article 145244.
- Wang, Q., Li, C., Zou, Y., Wang, H., Yi, T., & Huang, C. (2012). A highly selective fluorescence sensor for tin (Sn^{4+}) and its application in imaging live cells. *Organic & Biomolecular Chemistry*, 10(33), 6740–6746.