



## Review article

# Recent trends and future perspectives of photoresponsive-based mercury (II) sensors and their biomaterial applications

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## ABSTRACT

Recent advancements in the field of photoresponsive-based mercury (II) sensors have witnessed a surge in research focused on enhancing detection capabilities. Leveraging innovations in materials science, particularly with quantum dots, nanomaterials, and organic semiconductors, these sensors exhibit improved selectivity and sensitivity. Beyond traditional applications, such as environmental monitoring, the integration of photoresponsive principles with emerging technologies like the internet of things (IoT) and wearable promises real-time and remote mercury (II) ion detection. The on-going efforts also explore multifunctional sensors and miniaturization for on-site applications, addressing current challenges and paving the way for broader commercialization. This dynamic landscape underscores the potential for these sensors to play a crucial role in ensuring the effective monitoring and management of mercury (II) levels in diverse settings.

## 1. Introduction

Mercury contamination remains a formidable global concern, posing serious threats to ecosystems and human health due to its persistence, toxicity, and ability to biomagnify in the food chain [1]. As anthropogenic activities continue to release mercury into the environment, effective monitoring and detection strategies are paramount for timely intervention and mitigation. In response to this imperative, recent years have witnessed a remarkable surge in research dedicated to the development of advanced sensing technologies, with a particular focus on photoresponsive-based mercury (II) sensors [2,3]. This comprehensive introduction navigates through the multifaceted landscape of mercury pollution, elucidating the environmental ramifications, traditional detection methodologies, and the evolving role of photoresponsive -based sensors in addressing the shortcomings of conventional approaches. The pervasive impact of mercury contamination spans terrestrial, aquatic, and atmospheric domains, making it a truly global environmental challenge [4–8]. Industrial processes, coal combustion, and artisanal gold mining are prominent sources of mercury emissions, contributing to its ubiquitous presence in air, water, and soil. Once released, mercury undergoes complex biogeochemical transformations, ultimately leading to the formation of methylmercury, a highly toxic compound that accumulates in organisms, posing severe health risks to both wildlife and human populations. Understanding the intricate pathways through which mercury cycles in the environment

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is essential for devising targeted and effective monitoring strategies [9–12].

Traditional methods for detecting mercury ions, including atomic absorption spectrometry and fluorescence-based techniques, have played crucial roles in understanding mercury distribution. However, the procedures often suffer from limitations such as high detection limits, complex sample preparation, and limited real-time capabilities. The urgency to overcome these challenges has fueled the exploration of alternative sensing technologies, propelling photoresponsive -based sensors to the forefront of mercury detection research. The unique capability of these sensors to convert light signals into electrical responses offers a paradigm shift in the quest for enhanced sensitivity, selectivity, and real-time monitoring [13–15]. The heart of this paradigm shift lies in the innovative use of materials. Quantum dots, nanomaterials, and organic semiconductors have emerged as key players in amplifying the performance of photoresponsive -based mercury sensors. Quantum dots, with their tunable electronic properties and high surface area, provide a platform for precise and efficient detection. Nanomaterials, on the other hand, offer increased sensitivity through their unique structural characteristics. Organic semiconductors contribute to the development of flexible and cost-effective sensor platforms, extending the reach of these technologies to diverse applications and environments [16,17].

The versatility of photoresponsive-based sensors goes beyond mere detection. The integration of these sensors with the internet of things (IoT) and wearable devices introduces a dynamic dimension to environmental monitoring. This amalgamation allows for real-time, remote, and continuous monitoring, transforming the static nature of traditional sampling methods [18]. The implications of this integration extend into various sectors, from industrial processes to ecological studies, promising a comprehensive approach to mercury ion detection. As we delve deeper into the recent trends of photoresponsive-based mercury sensors, it becomes evident that these innovations not only address current detection challenges but also lay the groundwork for future advancements [19,20]. The following pages will unravel the intricate developments in sensor design, material synthesis, and the evolving applications of photoresponsive-based mercury (II) sensors (1). Through this exploration, we aim to elucidate the potential pathways that may shape the future of mercury sensing technologies and their broader implications for environmental sustainability and public health. This study looks at current developments in the synthesis, a design concept with photophysical characteristics, sensing mechanism, and analyte identification investigations with many parameters of photoresponsive-based mercury (II) sensors with a focus on biological applications (Fig. 1).

## 2. Azobenzene-based mercury ( $\text{Hg}^{2+}$ ) sensor

The azobenzene derivative with 1,3,4-triazole units as the basis for a highly sensitive fluorescent probe (2) for the selective detection of mercury has been devised, synthesized, and tested for its ability to recognize cations by UV–vis fluorescence. In DMF aqueous environments, the fluorescent probe shows a very selective response of fluorescence increase toward mercury (Fig. 2a) [21]. In addition, the two novel very specific colorimetric chemosensors (3) for  $\text{Hg}^{2+}$  have been developed and synthesized. They are based on azobenzene and highly selective  $\text{Hg}^{2+}$ -promoted deprotection of a dithioacetal. The sensor's color changes from pale yellow to deep red, which is readily visible to the naked eye in the presence of as little as 20  $\mu\text{M}$   $\text{Hg}^{2+}$ . Intramolecular charge transfer (ICT) is the fundamental signaling process. The  $\text{Hg}^{2+}$  selectivity of the sensors is good for several typical alkaline substances, alkaline earth, and transition metal ions. Moreover, they don't require any extra equipment to be used for in-field measurements using a dipstick method (Fig. 2b) [22].

The development and characterization of a novel family of azobenzene dyes (4) based on the internal charge transfer (ICT) mechanism allowed for the colorimetric and ratiometric detection of  $\text{Hg}^{2+}$ . In an aqueous methanol solution, the molecules containing azo and imino group functions may work in concert with  $\text{Hg}^{2+}$  to produce a significant blue shift from 453 to 363 nm, which

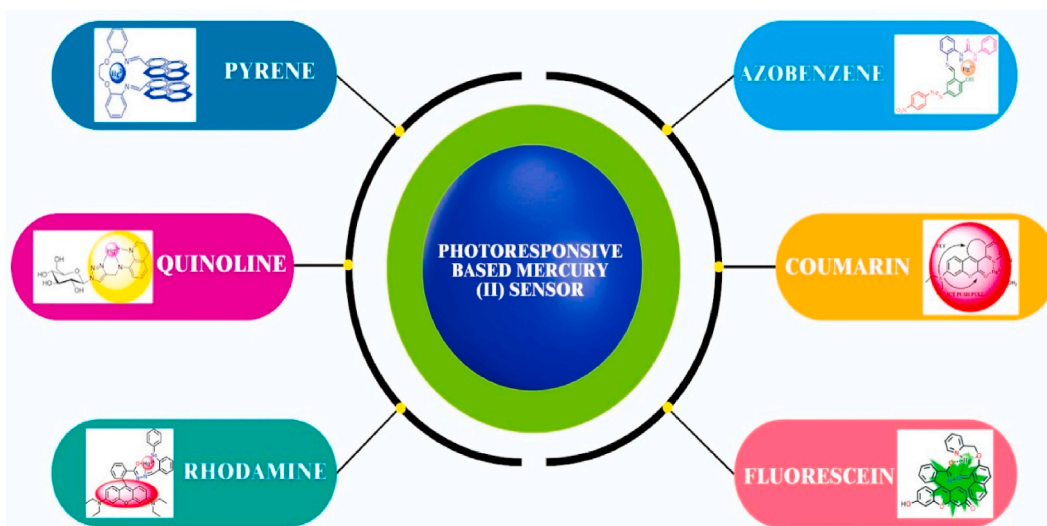
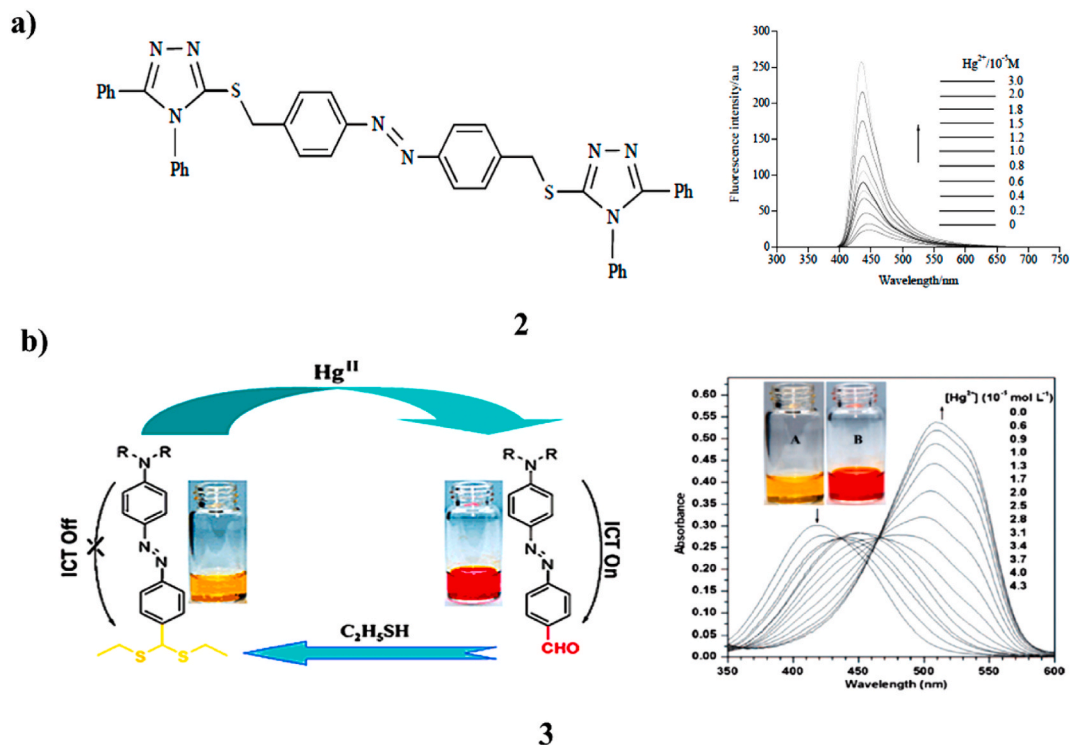
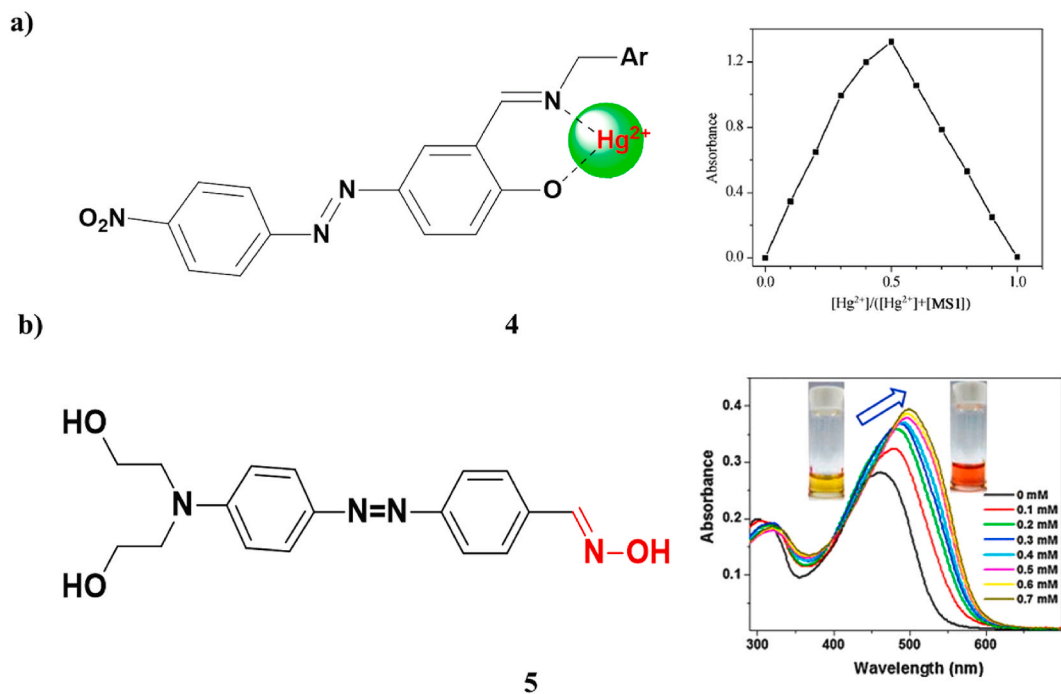


Fig. 1. Schematic representation of photoresponsive-based mercury (II) sensor.



**Fig. 2.** a). Fluorescence analysis of Azobenzene-Based Fluorescent Mercury Sensor (2). b). Absorbance analysis of Azobenzene-Based Colorimetric Chemosensors (3).



**Fig. 3.** a). Ratiometric study of azobenzene dye colorimetric and chemosensors (4). b). Structure of Aldoxime-functionalized azobenzene-based molecular probe Detection of Mercury and Fluoride ions (5).

corresponds to a noticeable shift in hue from orange to light yellow. This effect can be used for  $\text{Hg}^{2+}$  detection with the naked eye. UV-Vis spectroscopy was used to examine the sensors' sensitivity, specificity, and binding mode to  $\text{Hg}^{2+}$  (Fig. 3a) [23]. A molecular probe (5) was created for the dual detection of  $\text{Hg}^{2+}$  and  $\text{F}^-$  ions, utilizing the recently discovered aldoxime chemistry. The azobenzene-containing probe (Azo-2) produced from aldoxime was created and examined. In a DMSO/ $\text{H}_2\text{O}$  combination, it demonstrated remarkable sensitivity and selectivity towards ions containing mercury via an  $\text{Hg}^{2+}$  ion-catalyzed dehydration process at  $\text{pH} = 5$ . With the addition of  $\text{Hg}^{2+}$  ions, the probe showed a 70 nm red shift in its wavelength of absorption maximum along with a light yellow to dark violet color shift in the solution. It's interesting to note that Azo-2 also showed strong sensitivity and selectivity for  $\text{F}^-$  ions in a DMSO solution. This was made possible by the deprotonation of oxime-OH caused by  $\text{F}^-$  ions and the ensuing creation of an energetically preferred  $\text{HF}_2^-$  species. Visible detection of the  $\text{F}^-$  ion was aided by the solution's color changing from pale yellow to a deep red. NMR spectroscopy using  $^1\text{H}$ - and  $^{19}\text{F}$  produced confirmation of the oxime-fluoride interaction and the production of  $\text{HF}_2^-$ . The whole process is reversible, as demonstrated by the reaction of the oxime anion produced by  $\text{F}^-$  in a DMSO solution with water molecules to revert to the originally protonated oxime (Fig. 3b) [24].

A thioacetal chemosensor (6) was created by synthesizing an azobenzene and carbazole moiety at the same time.  $\text{Hg}^{2+}$  was shown to be able to specifically elicit changes in both color and fluorescence among other metal ions.  $^1\text{H}$  NMR measurements validated the mechanism of  $\text{Hg}^{2+}$ -promoted cleavage of thioacetal. The yellow  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solution turned into a colorless solution when  $\text{Hg}^{2+}$  was added. This precipitated as a mercuric salt and left behind an azobenzene-containing thioglycolamide (Fig. 4a) [25]. A novel set of benzoyl-thiourea derivatives (7) was synthesized, and their chemo-dosimetric responses to metal cations were examined in room-temperature aqueous solutions. Only  $\text{Hg}^{2+}$  ions showed reactions to permanent color changes in receptors among the several metal cations that were studied, as well as characteristic blue shifts in UV/vis spectra. The  $\text{Hg}^{2+}$  ion may be monitored using the receptors in a water-based solution having a pH range of 4–9 (Fig. 4b) [26].

The azo chromophore and phenylthiourea construction optical probes (8) were created and used for  $\text{CN}^-$  and  $\text{Hg}^{2+}$  detection with the naked-eye. The produced probes responded differently to  $\text{CN}^-$  and  $\text{Hg}^{2+}$  ions in terms of colorimetry.  $^1\text{H}$  NMR titration measurements were used to study the mechanism of the probe's binding interaction between  $\text{CN}^-$  and  $\text{Hg}^{2+}$  ions. The chemosensor's limit of detection and Job's plot analysis indicated that the stoichiometric ratios for  $\text{Hg}^{2+}$  and  $\text{CN}^-$  ions were respectively 1:1 (LOD = 4.89  $\mu\text{M}$  and 1:2 (LOD = 2.23  $\mu\text{M}$ ) (Fig. 5a) [27]. The developed and synthesized a novel straightforward fluorescent probe BAA (9) for  $\text{Hg}^{2+}$  in aqueous solution. By using fluorescence spectra, may be utilized to selectively identify  $\text{Hg}^{2+}$  in an aqueous solution over other common metal ions. The confirmation of the BAA's sensing mechanism towards  $\text{Hg}^{2+}$  was obtained using titration spectra, ESI-MS, and DFT calculations. With  $\text{Hg}^{2+}$ , the probe BAA showed a 1:1 binding mode. There was a reversible interaction between BAA and  $\text{Hg}^{2+}$ . In addition, the BAA had a quick reaction to  $\text{Hg}^{2+}$  and could detect  $\text{Hg}^{2+}$  throughout a broad pH range (3-10). Ultimately, the

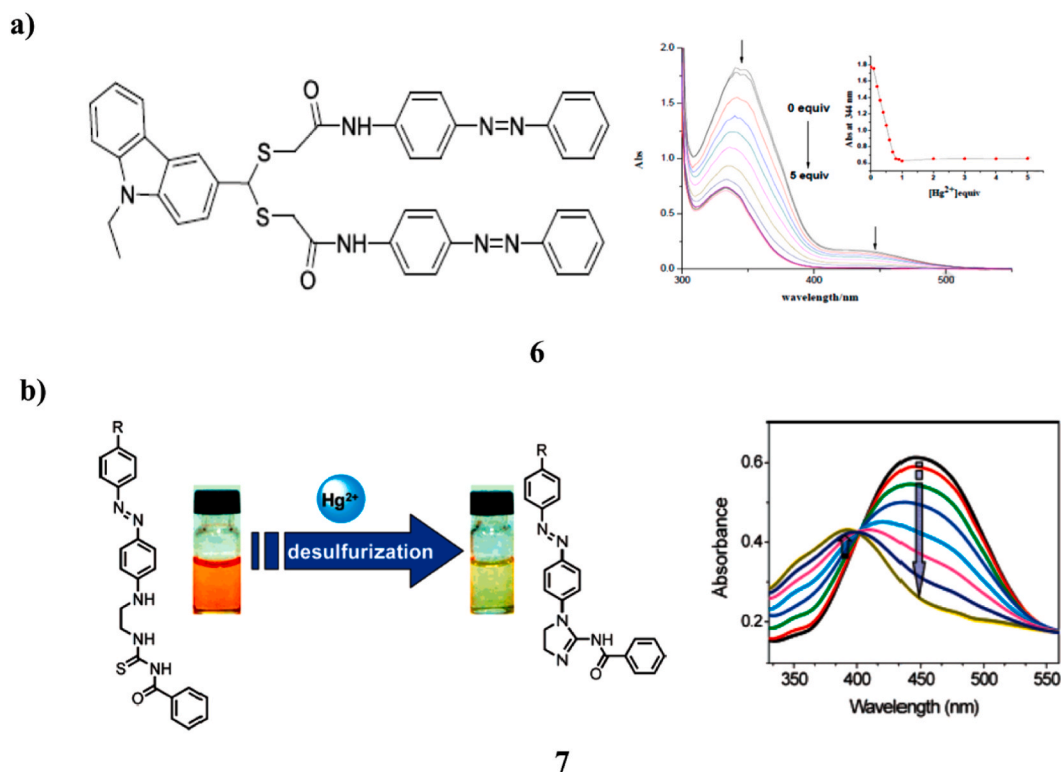


Fig. 4. a). Photophysical study of thioacetals based fluorogenic chemosensor for  $\text{Hg}(\text{II})$  (6). b). Absorption study of chemodosimetric detection of  $\text{Hg}(\text{II})$  (7).

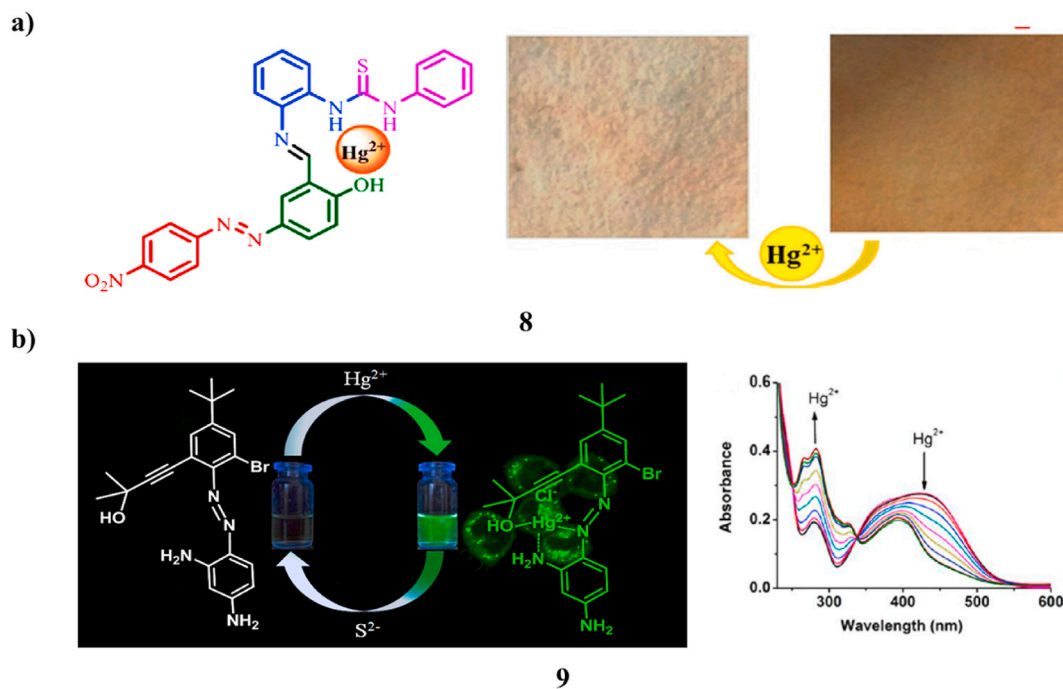


Fig. 5. a). Absorption study of azo-benzylidene-thiourea chemosensor (8). b). HOMO-LUMO energy gap study of fluorescent probe for  $\text{Hg}^{2+}$  (9).

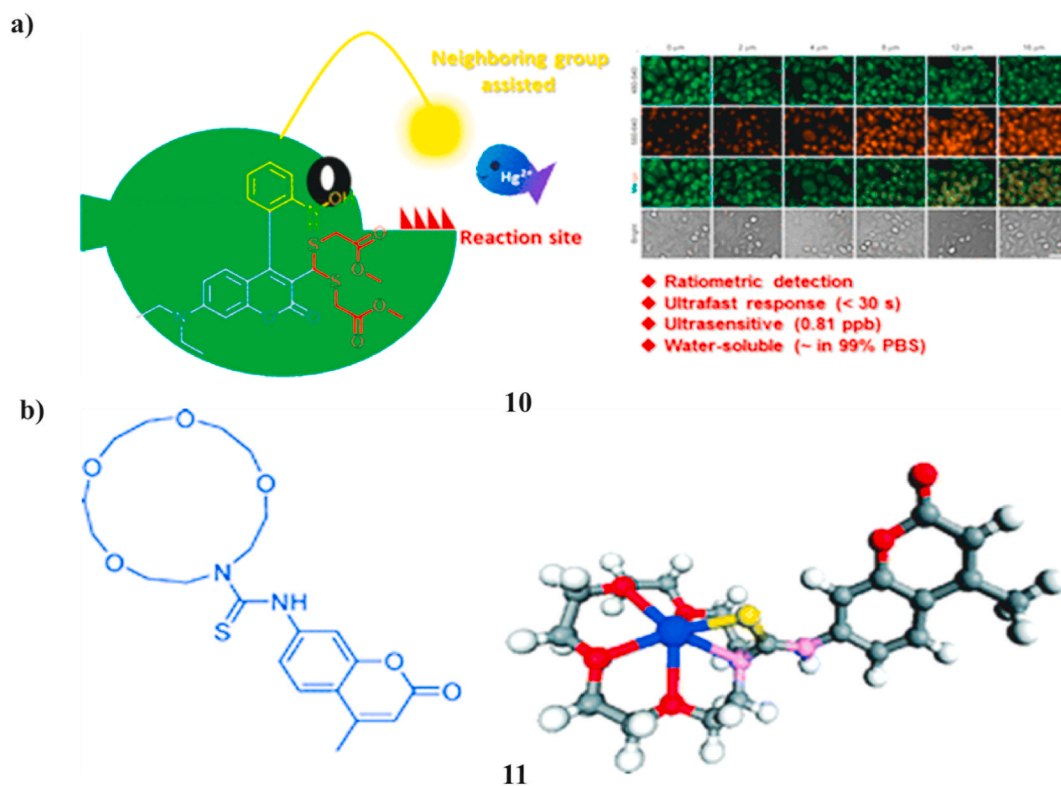


Fig. 6. a). Live cell imaging studies of Coumarin-Based  $\text{Hg}^{2+}$  Fluorescent Probe (10). b). PET study of coumarin-based fluorescent sensor (11).

probe was also effectively used to image  $\text{Hg}^{2+}$  ions in MCF-7 live cells and detect  $\text{Hg}^{2+}$  in the water from the lake samples (Fig. 5b) [28].

Azobenzene-based mercury (II) sensors operate through the reversible photoisomerization of azobenzene groups, which alters the optical properties of the sensor upon mercury (II) ion binding. The binding induces a change in the azobenzene's geometric configuration from trans to cis, resulting in a detectable shift in UV-Vis absorbance or fluorescence. This mechanism offers high sensitivity and selectivity due to the strong interaction between mercury ions and azobenzene. The sensors have notable advantages, including their high sensitivity, low detection limits, and potential for integration into IoT and wearable devices for real-time monitoring. However, challenges include stability issues and the need for complex fabrication processes. Case studies, such as the integration of azobenzene sensors in wearable health monitoring devices, highlight their potential in environmental and personal health applications, demonstrating their effectiveness in detecting trace mercury levels and contributing to enhanced safety and environmental monitoring.

### 3. Coumarin-based mercury ( $\text{Hg}^{2+}$ ) sensor

A new ultrasensitive ratiometric fluorescence probe has been created to detect mercury ions through the particular desulfurization of dithioacetal that is activated by mercury. In an aqueous solution, this probe (10) demonstrates an effective color response and fluorescence in response to  $\text{Hg}^{2+}$ . It is superior to most reported ones due to its quick response kinetics, low limit of detection ( $\sim 0.81$  ppb), high selectivity, and visible light emission (450–650 nm). The application of it to ratiometrically  $\text{Hg}^{2+}$  pictures in living HeLa cells has been executed easily (Fig. 6a) [29]. A quick and high-yield synthetic process was used to develop and create a water-soluble, fluorescent ion probe (11) with excellent selectivity for  $\text{Hg}^{2+}$  ions. The probe is a member of the turn-on sensor family. It operates by the process of photoinduced electron transfer, producing a dye that may be used as a tool for the identification and measurement of mercury in biological and environmental samples (Fig. 6b) [30].

Triazolyl coumarin derivatives (12) were synthesized as fluorescence sensors to investigate their selectivity and binding ability toward metal ions. These derivatives included spacer groups between the coumarin and triazole groups and ones without. With fluorescence intensification, it demonstrated a remarkable selectivity toward  $\text{Hg}^{2+}$  in polar protic solvents MeOH- $\text{CHCl}_3$ . Moreover, it was shown to bind two  $\text{Hg}^{2+}$  at a high concentration ( $>12.5$  mM) of  $\text{Hg}(\text{ClO}_4)_2$ . It displayed a binding stoichiometry concerning a single  $\text{Hg}^{2+}$ . Based on the findings of the ligands'  $^1\text{H}$  NMR titration, IR, and fluorescence sensing (Fig. 7a) [31]. The development of a novel colorimetric and fluorescent chemosensor (13) based on 7- (diethylamino)-3- (pyrimidin-4-yl)-2H-chromen-2-one (PYC) has been proposed and made feasible the detection of  $\text{Hg}^{2+}$  in the presence of other competing metals in mixed aquatic environments. When exposed to  $\text{Hg}^{2+}$ , the PYC's color changes from green to red to a yellow-green color to light orange in fluorescence. The absorption spectra also exhibit a redshift of around 80 nm in wavelength. Test strips 15 based on PYC were created to serve as practical

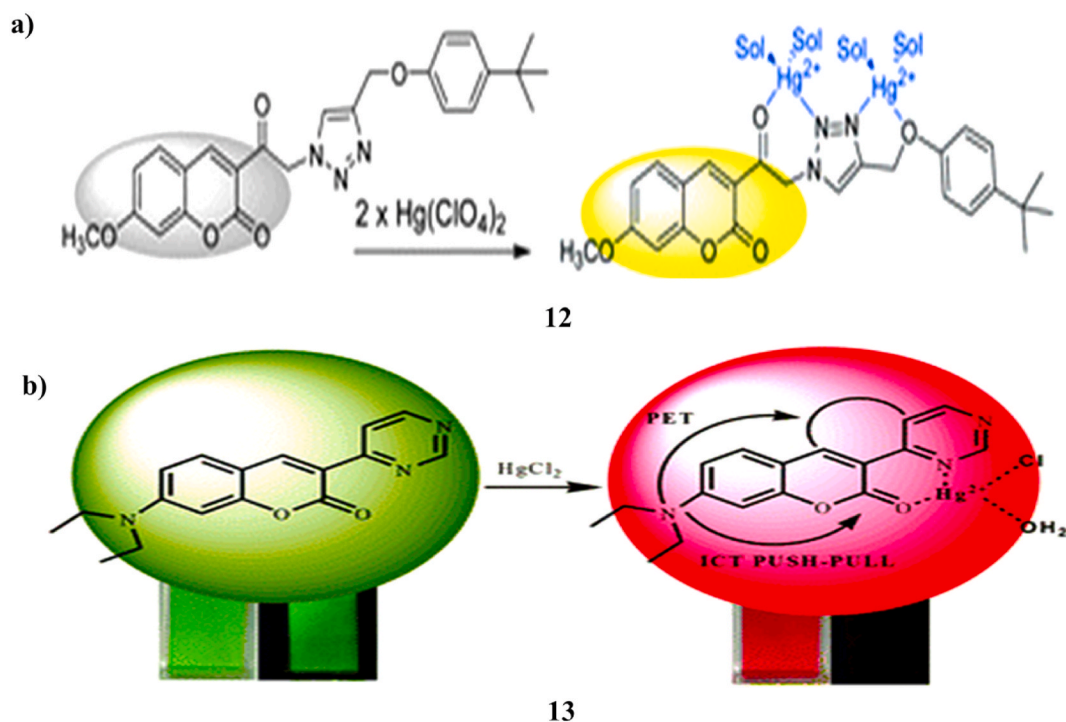


Fig. 7. a). Mechanism of triazolyl coumarins based  $\text{Hg}^{2+}$  chemosensors (12). b). ICT study of Coumarinyl-appended Pyrimidine based Colorimetric  $\text{Hg}^{2+}$  Sensor (13).

and effective  $\text{Hg}^{2+}$  test kits (Fig. 7b) [32].

A novel colorimetric and ratiometric fluorescent chemo-dosimeter (14) based on intramolecular charge transfer (ICT) has been logically conceived and established for the detection of  $\text{Hg}^{2+}$ . The probe functions through the particular desulfurization process of thiocoumarin to coumarin, which is encouraged by mercury. It demonstrates a low LOD of 1.85 ppb and great selectivity and sensitivity in a nearly pure water solution. Moreover, it was effectively employed for  $\text{Hg}^{2+}$  fluorescence imaging in living cells (Fig. 8a) [33]. The method of 7-hydroxycoumarin phototautomerism in an aqueous solution served as the foundation for the creation of a novel luminous polymer (15) for  $\text{Hg}^{2+}$  detection. The developed method showed higher sensitivity and selectivity towards  $\text{Hg}^{2+}$  in acetonitrile/water combination compared to several other metal ions with significant suppression of the principal emission band in fluorescence. It was shown that the 7-hydroxycoumarin photo-tautomers chemical equilibrium is changed in the presence of  $\text{Hg}^{2+}$  by the excited state of the intramolecular proton exchange (ESIPT) mechanism, which results in a ratiometric fluorescence response after stepwise addition of  $\text{Hg}^{2+}$ . A comparison of the initial alkynylated coumarin's  $^1\text{H}$  NMR spectra in polar and non-polar aprotic solvents explained the happening of the ESIPT process. Further confirmation of this came from the  $^1\text{H}$  NMR of 4 obtained by adding  $\text{Hg}^{2+}$  gradually in polarised aprotic solvent. Titration experiments revealed a higher sensitivity with a threshold for detection at the nanomolar level (50 nM) as well as a faster and reversible reaction. The created systems practical uses were examined using actual samples, yielding positive outcomes for both freshwater and lakeside samples (Fig. 8b) [34].

The design and manufacture of fluorescence-based devices for in-field  $\text{Hg}^{2+}$  detection and screening for ecological and industrial samples remains a tough problem, even though fluorescent sensing molecules have been suggested and investigated to indicate  $\text{Hg}^{2+}$  ion binding. Three novel coumarin-based fluorescent chemosensors (16) with mixed thia/aza macrocyclic frameworks as receptor units have been synthesized and characterized. By revealing an OFF-ON selective response to  $\text{Hg}^{2+}$  ions in MeCN/ $\text{H}_2\text{O}$ , these probes made it possible to image this metal ion in Cos-7 cells when performed *in vitro*. When ligands are reinforced on polyvinyl chloride (PVC)-based polymeric membranes or incorporated into silica core-polyethylene glycol (PEG) shell nanoparticles, they may also detect  $\text{Hg}^{2+}$  ions in pure water with selectivity. Specifically, an optical detecting array based on the computer's screen photo-assisted method (CSPT) was created, utilizing the fluorescence characteristics of ligands. The device responds quantitatively to  $\text{Hg}^{2+}$  ions in samples of natural water when the ligand is distributed across PVC membranes (Fig. 9a) [35]. The Cu(I) catalyzed Huisgen cycloaddition to create a triazole-bridged coumarin conjugated quinoline sensor (17) that showed excellent selectivity for hazardous  $\text{Hg}^{2+}$ . Remarkably, a time-resolved fluorescence analysis has shown that no indication of the transfer of energy from the quinoline molecule

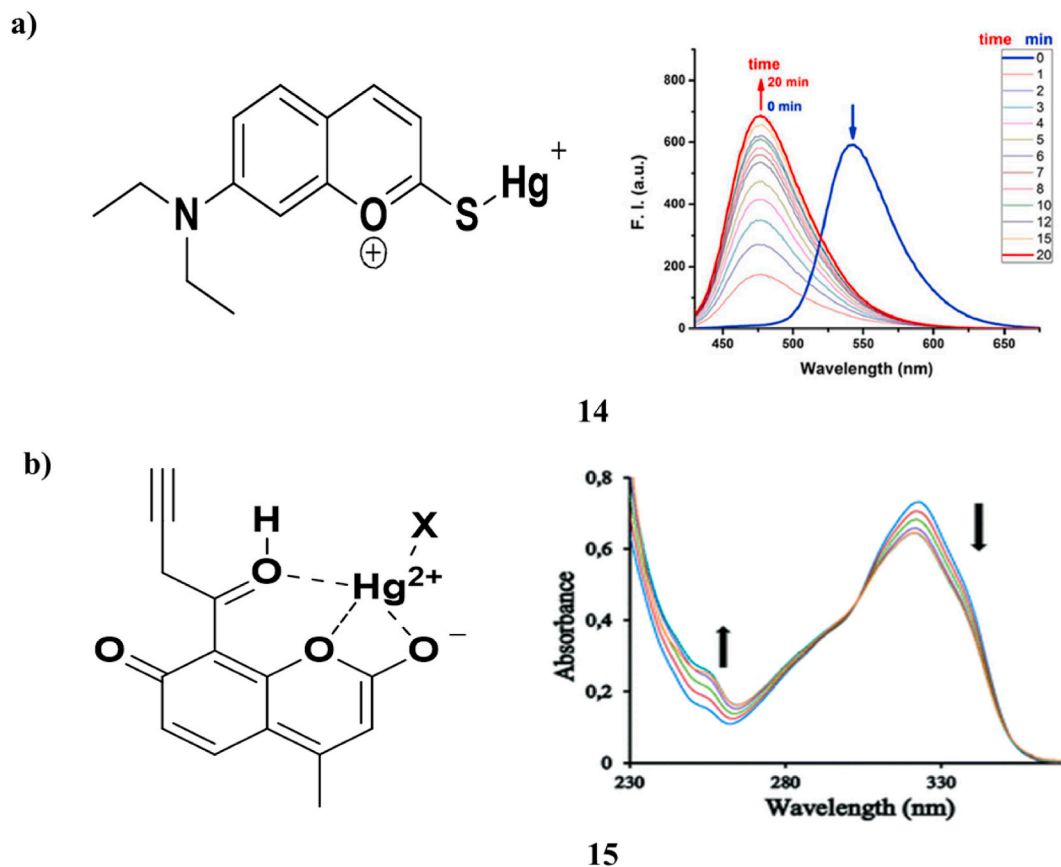


Fig. 8. a). Live-Cell Imaging of Thiocoumarin-Based Colorimetric  $\text{Hg}^{2+}$  sensor (14). b). Mechanism of coumarin-triazole polymer-based ESIPT-based  $\text{Hg}^{2+}$  detection (15).

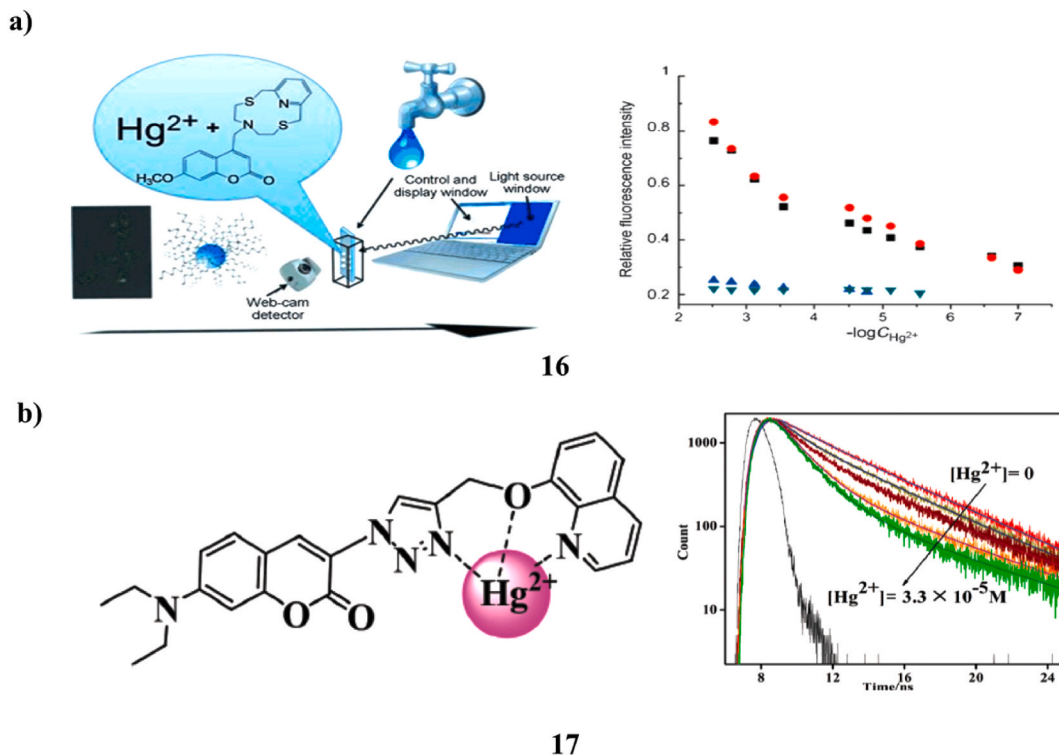


Fig. 9. a). Fluorescence studies of Coumarin-Based Luminous  $\text{Hg}^{2+}$  Chemosensors (16). b). FRET studies of triazole bridged coumarin-hydroxyquinoline based  $\text{Hg}^{2+}$  sensor (17).

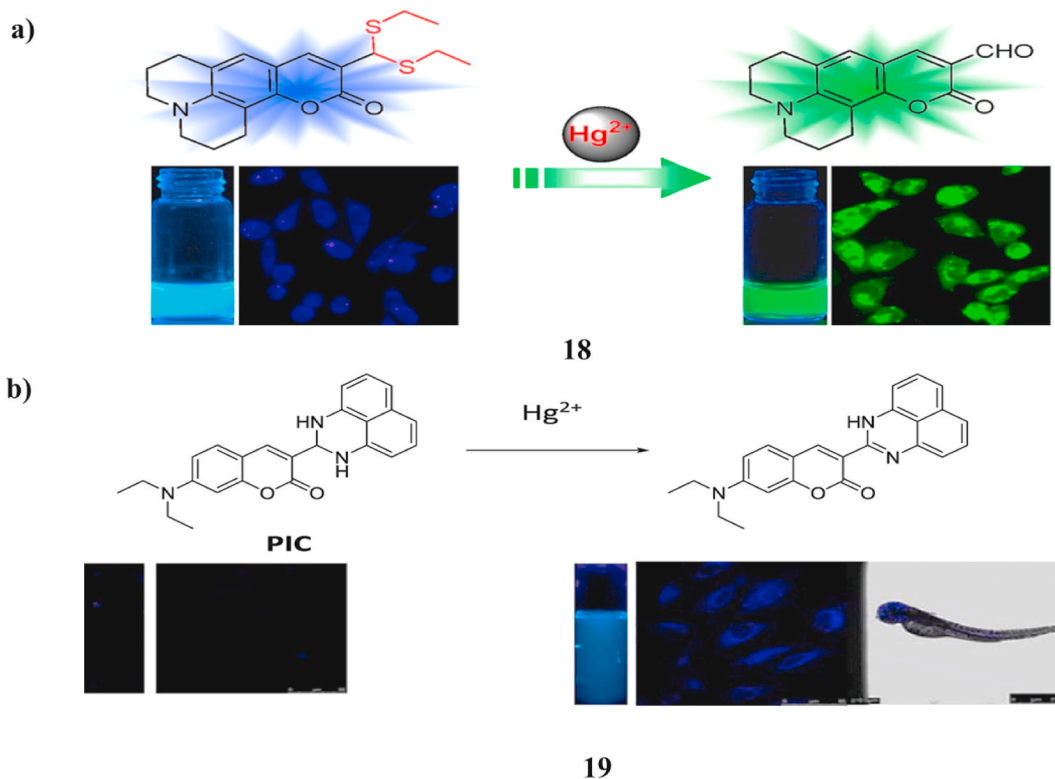
to coumarin has been discovered. TDDFT simulations corroborate the potential binding mechanism of this sensor to  $\text{Hg}^{2+}$ , which has been determined by NMR analysis, steady-state and time-resolved fluorescence spectroscopy, and other methods. Because the sensor is non-toxic and permeable to cell membranes, it can be used for intracellular  $\text{Hg}^{2+}$  detection (Fig. 9b) [36].

Novel reactive fluorescent probes (18) towards ions composed of mercury were created by utilizing the well-known coumarin chromophore and the unique  $\text{Hg}^{2+}$ -promoted deprotection process of dithioacetals. It showed impressive fluorescence quenching with the incorporation of mercury ions, which helped to provide a strong signal output throughout the sensing process. However, its fluorescence (60 nm) and absorption (60 nm) spectra both displayed a notable red shift with a detection limit of 90 nM. It responded preferentially to  $\text{Hg}^{2+}$  under this particular chemical reaction, and changes in the apparent absorption and emission spectra could only be caused by the addition of  $\text{Hg}^{2+}$ . Furthermore, it was effectively used in ratiometric fluorescent techniques for microscopic imaging to detect  $\text{Hg}^{2+}$  in HeLa cells (Fig. 10a) [37]. A perimidine moiety was included in the design and synthesis of a reaction-based fluorescent probe PIC (19) intended for  $\text{Hg}^{2+}$  detection. At physiological pH, it can preferentially separate  $\text{Hg}^{2+}$  with a 42-fold fluorescence amplification from the remaining metal ions. The upper detection limit of  $\text{Hg}^{2+}$  with this probe is 1.08  $\mu\text{M}$ . It may be used to detect  $\text{Hg}^{2+}$  in blue-emitting cells in real-time (Fig. 10b) [38].

A novel coumarin-based N-[4-(2-Oxo-2H-chromen-3-yl)-thiazol-2-yl] was successfully synthesized for the first time. The fluorescent monomer of acrylamide (OCTAA) was achieved. When metal ions are present, the fluorescence characteristics of the OCTAA monomer (20) are quenched. The polymerization was verified by the use of  $^{13}\text{C}$  NMR and FTIR spectroscopy. The purpose of the investigation using X-ray photoelectron spectroscopy is to assess the functional groups engaged in the complexation process with mercury. IIP's morphology was examined using the FE-SEM. The BET surface area of NIP and IIP was found to be  $48.1 \text{ m}^2 \text{ g}^{-1}$  and  $76.90 \text{ m}^2 \text{ g}^{-1}$  in nitrogen adsorption-desorption studies. With a response spectrum that is linear ranging from 0.05 to 1.2  $\mu\text{mol L}^{-1}$  and a limit of detection of 0.020  $\mu\text{mol L}^{-1}$ , the IIP fluorescence was recorded at 450 nm. Mercury was effectively detected from a genuine water sample using the fluorescent  $\text{Hg}(\text{II})$ -IIP (Fig. 11a) [39]. A novel fluorescence sensor (21, PPC-S) for  $\text{Hg}^{2+}$  that relies on the coumarin chromophore based on pyrazolo[3,4-b]pyridine aggregation-induced emission (AIE) (PPC-O). PPC-S that is AIE inactive after the desulfurization process with  $\text{Hg}^{2+}$  may be converted to PPC-O that is AIE active. This PPC-O can then be used for the fluorescence turn-on detection of  $\text{Hg}^{2+}$  in aqueous solutions with appropriate selectivity and sensitivity (Fig. 11b) [40].

Mercury has long been recognized to have detrimental effects on biological health, which is why the creation of fluorescent sensors (22) for  $\text{Hg}^{2+}$  has received a lot of interest. Using time-dependent density functional theory, the optical characteristics of two recently synthesized  $\text{Hg}^{2+}$  chemical sensors based on the coumarin-rhodamine system were thoroughly examined. It is demonstrated that Probes are efficient ratiometric fluorescent  $\text{Hg}^{2+}$  probes that identify  $\text{Hg}^{2+}$  via bond energy transfer processes and Förster resonance energy transfer, respectively. Thus, it is shown how the spacer group between the acceptor and the donor affects the probe's ability to sense. In particular, these two probes' two-photon absorption characteristics are computed. Significant two-photon responses are seen





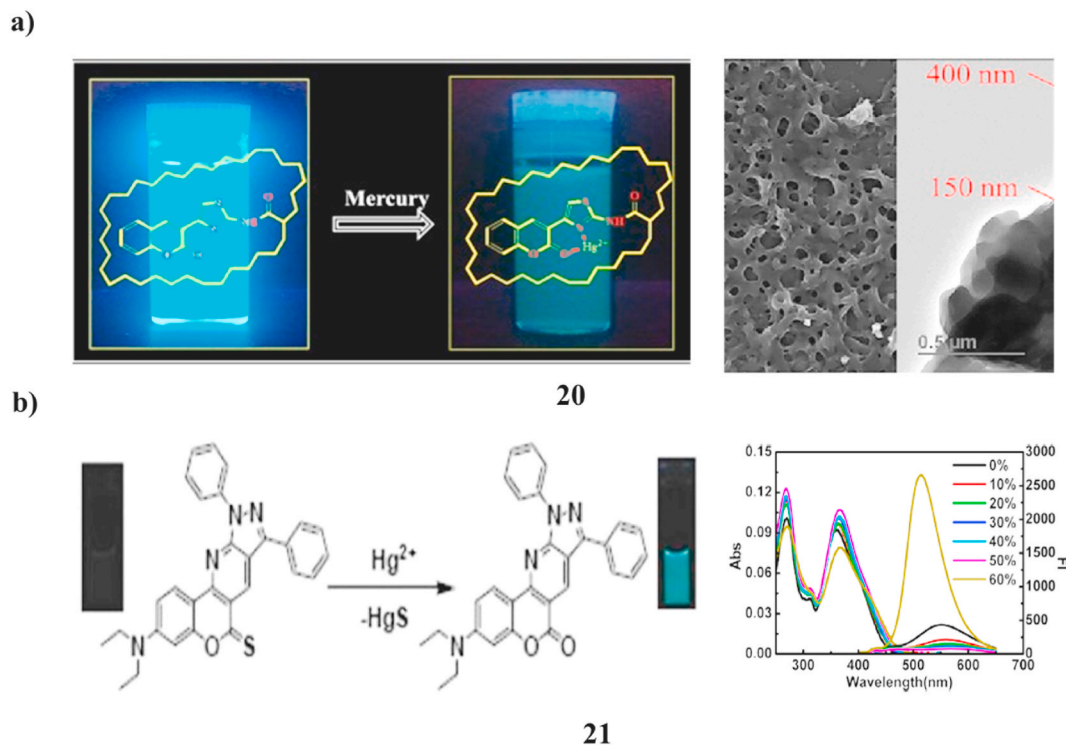
**Fig. 10.** a). Bioimaging studies of Thioacetalized coumarin-based fluorescent sensor (18). b). Zebrafish studies of Coumarin-based  $\text{Hg}^{2+}$  fluorescent sensor (19).

by the probes in the near-infrared light spectrum. However, the presence of  $\text{Hg}^{2+}$  only significantly increases Probe's maximum two-photon absorption cross-section, suggesting that Probe may be used as a two-photon stimulated fluorescent probe for  $\text{Hg}^{2+}$ . Theoretical research might establish a connection between the optical characteristics and probe structure, offering insights into the creation of effective two-photon fluorescence sensors for in vivo biological imaging of  $\text{Hg}^{2+}$  (Fig. 12) [41].

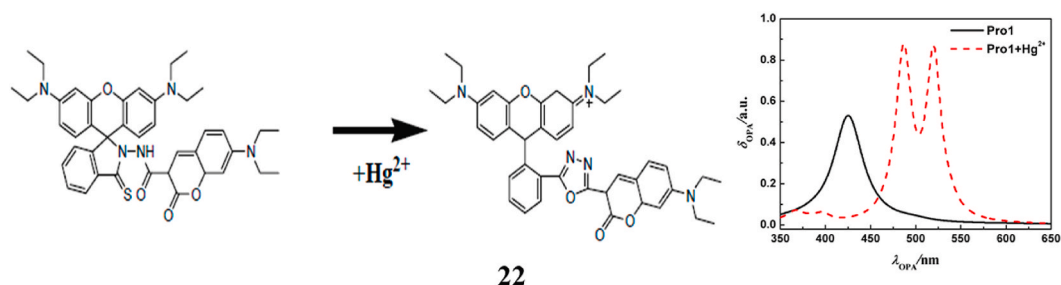
Coumarin-based mercury (II) sensors operate primarily through fluorescence quenching or colorimetric changes upon mercury ion binding, exploiting the chelating properties of coumarin derivatives. The sensing mechanism involves mercury (II) ions coordinating with the coumarin-based ligands, leading to a measurable decrease in fluorescence or a color shift due to altered electronic states. These sensors are advantageous due to their high sensitivity, rapid response, and ease of functionalization. However, they face limitations such as potential interference from other metal ions and limited stability under harsh conditions. In real-world applications, such as IoT and wearable devices, coumarin-based sensors have been integrated into water quality monitoring systems and environmental sensing devices, demonstrating their practical utility and effectiveness in continuous, remote, and real-time detection.

#### 4. Fluorescein-based mercury ( $\text{Hg}^{2+}$ ) sensor

Two rhodamine B fluorophores are linked to a fluorescein-based fluorescent chemosensor and "naked-eye" indicator (23) via hydrazide moieties. It was created and manufactured to detect  $\text{Hg}^{2+}$  with extreme sensitivity and selectivity. The fluorescein energy donor and the ring-opened rhodamine B receivers were connected to the sensor system via the FRET mechanism. Both fluorescence amplification and a chromogenic shift (from monochrome to pink) were indicative of the binding to  $\text{Hg}^{2+}$ . It is demonstrated that the sensor can distinguish between different foreign metal ions, with a detection limit of  $2.02 \times 10^{-8}$  M for  $\text{Hg}^{2+}$  (Fig. 13a) [42]. The synthesis of a fluorescein hydrazone-based conjugate (24) involves the coupling of fluorescein hydrazide with 2-(Pyridin-2-ylmethoxy)-naphthalene-1-carbaldehyde. It may be characterized using a variety of spectroscopic methods, including IR,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, and ESI-MS. In comparison to other metal ions, it demonstrated a high degree of sensitivity and selectivity towards hazardous  $\text{Hg}^{2+}$  ions in the semi-aqueous medium. Notably, the emission of fluorescence centered at 520 nm was found to be significantly enhanced due to the ring opening of the spirolactam molecule in the fluorescein structure brought on by  $\text{Hg}^{2+}$ . The binding constant of  $\text{Hg}^{2+}$  was determined to be  $(0.43 \pm 0.04) \times 10^4 \text{ M}^{-1}$  with detection limits of 1.24  $\mu\text{M}$ . The 1:1 binding of  $\text{Hg}^{2+}$  was established using Job's technique and validated by ESI-MS tests. Due to a larger binding force among  $\text{Hg}^{2+}$  and  $\text{S}^{2-}$ ,  $\text{S}^{2-}$  grabbed the  $\text{Hg}^{2+}$  in the complex, quenching the intensity of the fluorescence. DFT experiments established the putative coordinated environment in the  $\text{Hg}^+$  complex. Instruments with logic gate functions can make use of the fluorescence "OFF-ON-OFF" mode, which was studied in the event of  $\text{Hg}^{2+}$  and  $\text{S}^{2-}$ . Additionally, they show little cytotoxicity and biocompatibility, making them appropriate for fluorescent cell visualization of



**Fig. 11.** a). Nanomolar study of Coumarin-based Fluorescent Hg(II) sensor (20). b). AIE activity of pyrazolo[3,4-b]pyridine-based coumarin chromophores (21).



**Fig. 12.** Theoretical Studies of Coumarin-Rhodamine based Hg<sup>2+</sup> Probes (22).

Hg<sup>2+</sup> ions in living HepG2 cells (Fig. 13b) [43].

The fluorescein-based fluorescent Hg<sup>2+</sup> sensor (25) that uses EDPMA as a receptor was created and used to successfully image Hg<sup>2+</sup> in live cells. It shows good selectivity and reactivity for detecting Hg<sup>2+</sup> with a 51-fold increase in aqueous solution, and it displays a characteristic fluorescein emission band at 539 nm (Fig. 14a) [44]. The synthesis of a new symmetrical diarylethene derivatives (26) with a fluorescein unit and its potential use as a fluorescent probe for the identification of metal ions in biological, industrial, and environmental materials were investigated. The 1:1 binding stoichiometry showed both extremely sensitive and selective colorimetric and fluorescence reactions toward Hg<sup>2+</sup>. When Hg<sup>2+</sup> was present, the derivative's fluorescence intensity increased noticeably, blue-shifting from 550 nm to 504 nm. Furthermore, it demonstrated several regulated transition patterns in response to chemical and light stimuli. A combinational logic gate function was built employing the intensity of fluorescence at 504 nm as the output and the light and chemical stimulation as the inputs, based on the fluorescence switching behaviors that were "OFF-ON-OFF" (Fig. 14b) [45].

The fluorescence probe fluorescein hydrazide (27) was created specifically for the fluorescence assay method of mercury sensing. When Hg<sup>2+</sup> ions were present, the probe was extremely luminescent and green in color, but it was colorless and non-fluorescent otherwise. In pH 12 buffer conditions, it is very selective to Hg<sup>2+</sup> ions. During the fluorimetric examination of the Hg<sup>2+</sup> ions, no other ions caused any interference. The excitation wavelength for the fluorescence test was 502 nm, while the emission wavelength was 520 nm. The amount of Hg<sup>2+</sup> ions present in the test solution is proportionate to the emission wavelength, which is measured at 520 nm. Lead acid battery samples were successfully subjected to mercury speciation using the established fluorescence test procedure, which employed fluorescein hydrazide as the fluorescent probe (Fig. 15a) [46]. A novel fluorescent sensor (28) was created and

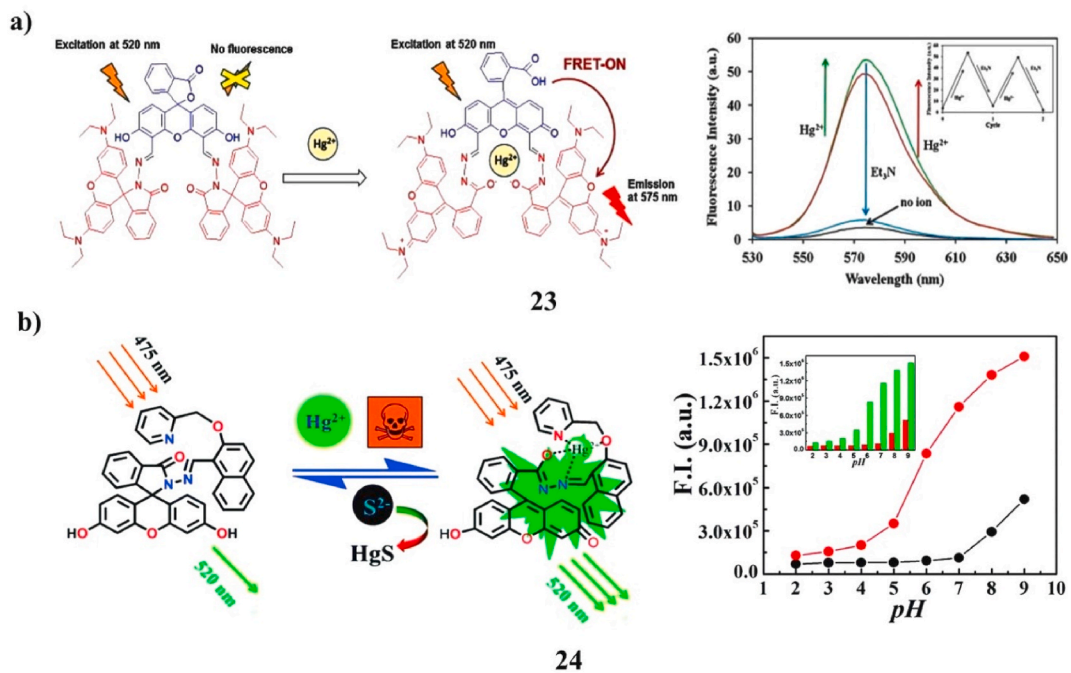


Fig. 13. a). FRET studies of fluorescent  $\text{Hg}^{2+}$ -sensor (23). b). Cell-Imaging studies of fluorescein-based  $\text{Hg}^{2+}$  chemosensor (24).

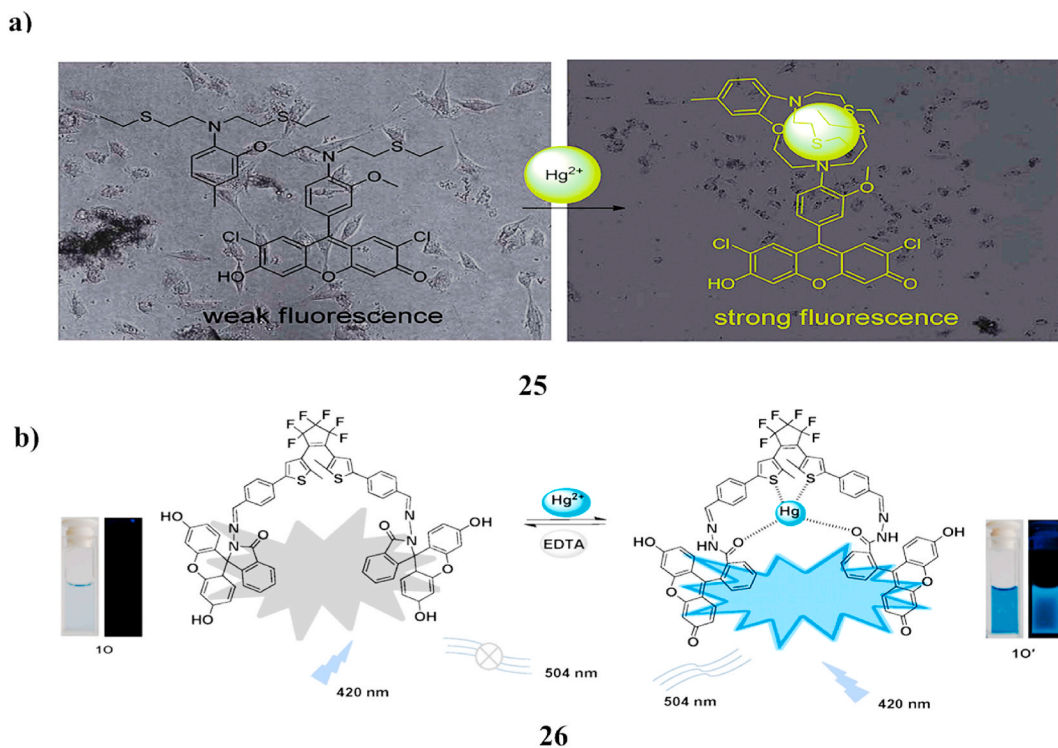
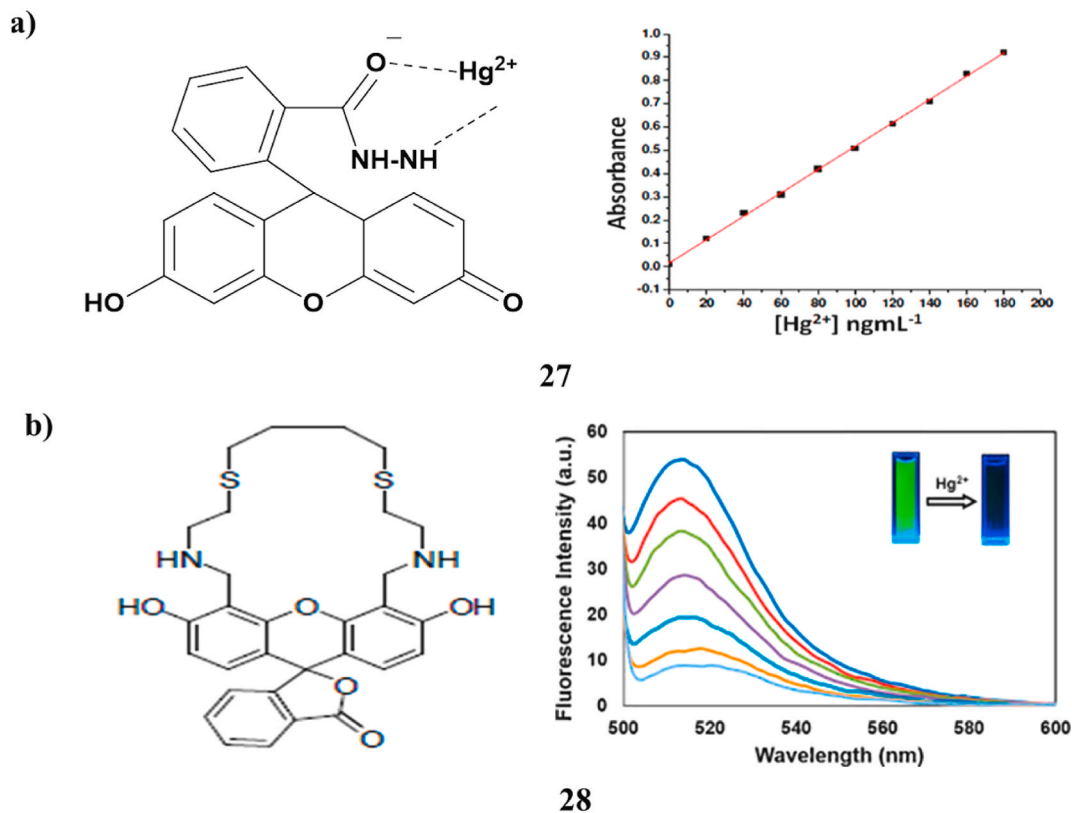


Fig. 14. a). Living cell imaging of Fluorescein-based fluorescent sensor (25). b). Photophysical study of fluorescein-linked diarylethene  $\text{Hg}^{2+}$  chemosensor (26).



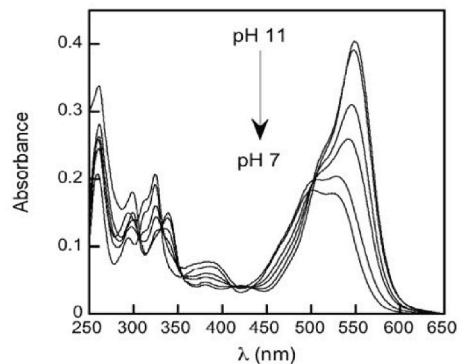
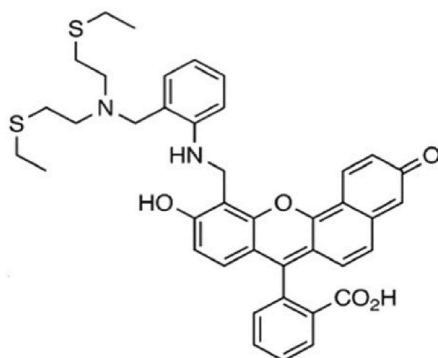
**Fig. 15.** a). Fluorescence study of fluorescein hydrazide based Mercury sensor (27). b). Biostudy of dithia-cyclic fluorescein  $\text{Hg}^{2+}$ -chemo-sensor (28).

manufactured as a fluoro-ionophore for the ocular and visual-eye detection of  $\text{Hg}^{2+}$  in a buffered aqueous solution. It is based on the fluorescein dithia-cyclic skeleton. Alkylation, ester hydrolysis, imine production, imine reduction, and Kornblum oxidation were used in its preparation. It was demonstrated that the sensor could distinguish between different interfering metal ions and offered highly sensitive and selective ON-OFF fluorescence detection toward  $\text{Hg}^{2+}$ . In addition, they demonstrated chromogenic alteration upon adhering to  $\text{Hg}^{2+}$ , acting as a "visual-eye" indication that was discernible by a discernible shift in the hue of the solution from yellow to orange in color. The sensor's  $\text{Hg}^{2+}$  detection limit was  $7.38 \times 10^{-9}$ , or 1.48 ppb, which was less than the amount that the US Environmental Protection Agency allowed to be present in drinking water (Fig. 15b) [47].

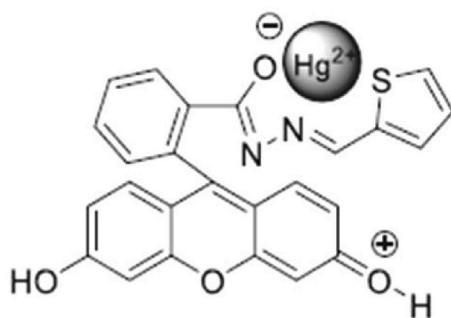
A red-emitting sensor for mercuric ions is given together with its synthesis, photophysical characteristics, and  $\text{Hg}(\text{II})$  binding. A thioether-rich metal-binding unit is used by Mercury Sensor (29, MS5), which is based on the seminaphthofluorescein chromophore. This sensor allows for the detection of  $\text{Hg}(\text{II})$  in an aqueous solution in both turn-on and single-excitation dual-emission ratiometric modes. It has a  $\text{Hg}(\text{II})$ -specific fluorescence response and is selective for  $\text{Hg}(\text{II})$  over alkali and alkaline earth metals, mainly divalent first-row transition metal ions. Recycling-friendly MS5 binds mercury (II) reversibly. The more modest threshold for detection of 50 nM is achieved by using a 500 nM probe, while the EC50 for 1  $\mu\text{M}$  MS5 is 910 nM. Additionally presented are X-ray crystallographic experiments utilizing a salicylaldehyde-based structure model for MS5. Research on naturally occurring water samples that have been tainted with mercuric salts shows that MS5 is capable of quickly identifying  $\text{Hg}(\text{II})$  in these complicated solutions, indicating its possible use in field applications (Fig. 16a) [48]. The cation-sensing characteristics of a straightforward colorimetric and turn-on fluorescence receptor FT (30) were developed and examined. In a DMSO/ $\text{H}_2\text{O}$  solution, receptor FT bound to  $\text{Hg}^{2+}$  and changed color selectively. The FT- $\text{Hg}^{2+}$  complex's association constant was determined to be  $3.03 \times 10^9 \text{ M}^{-1}$ , and the  $\text{Hg}^{2+}$  detection limit was discovered to be 0.24 ppm (Fig. 16b) [49].

Fluorescein-based mercury (II) sensors operate on a fluorescence quenching mechanism, where the presence of  $\text{Hg}^{2+}$  ions leads to a significant decrease in fluorescence emission due to the interaction between the ions and the fluorescein dye. This quenching effect results from the formation of a complex that disrupts the dye's fluorescence properties. Advantages include high sensitivity and selectivity towards mercury ions, along with a relatively straightforward sensor design. However, limitations involve potential interference from other metal ions and limited stability under diverse environmental conditions. In real-world applications, such as IoT-enabled water quality monitoring and wearable devices for environmental safety, these sensors provide valuable, real-time detection of mercury contamination, enhancing both public health and safety management. Case studies highlight their use in environmental monitoring systems, demonstrating their effectiveness in detecting trace levels of mercury in industrial and natural waters.

a)

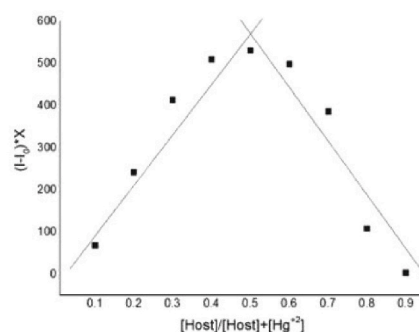


b)



29

30



**Fig. 16.** a). Photophysical properties of seminaphthofluorescein mercury sensor (29). b). Photophysical study of thiophene-based fluorescein-hydrazone derivative for  $\text{Hg}^{2+}$  Chemosensor (30).

### 5. Pyrene based mercury ( $\text{Hg}^{2+}$ ) sensor

A sensor for Mercury ions ( $\text{Hg}^{2+}$ ), utilizing a bottom gate top contact organic thin film transistor (OTFT), was successfully fabricated. Pyrene, including a thiol group with a significant affinity for  $\text{Hg}^{2+}$  ions, was used to functionalize the OTFT channel region. The OTFT sensor (31) exhibited a charge mobility of  $0.28 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , a threshold voltage of  $-22.3 \text{ V}$ , and an on-to-off ratio of  $10^3$ . Compared to the other two valence metal ions, the sensor exhibits strong selectivity for  $\text{Hg}^{2+}$  ions. When being subjected to various concentrations of  $\text{Hg}^{2+}$  ions, ranging from  $1 \text{ mM}$  to  $0.01 \text{ }\mu\text{M}$ , the OTFT sensor demonstrated a high sensitivity to  $\text{Hg}^{2+}$  ions, as evidenced by an increase in drain current. In addition, the practical significance of the OTFT sensor was showcased by its capacity to detect the presence of  $25 \text{ }\mu\text{M}$   $\text{Hg}^{2+}$  ion in tap, drinking, and ocean samples (Fig. 17a) [50]. The  $\text{Hg}^{2+}$  was detected by synthesizing a new long-wavelength turn-on fluorescence chemosensor (32, CS) based on pyrene. It could efficiently detect  $\text{Hg}^{2+}$  and generate the turn-on fluorescence emission at  $607 \text{ nm}$  under the presence of other metallic ions. In addition, there was a red shift in the absorption spectra. However, the naked eye was able to immediately witness the solution's color change from yellow to orange. The job plot, the results from electrospray ionization mass spectrometry, microscopy with scanning electrons, and calculations using density functional theory all supported the connection between CS and  $\text{Hg}^{2+}$ . It was discovered that adding  $\text{I}^-$  to the CS and  $\text{Hg}^{2+}$  solution might cause the fluorescence of CS to be reversible. CS demonstrated excellent sensitivity and great selectivity for  $\text{Hg}^{2+}$ , with a  $36 \text{ nm}$  detection limit. In addition, CS might be used to detect  $\text{Hg}^{2+}$  using silica gel plates and test strips (Fig. 17b) [51].

A novel derivative of bispyrenyl azadiene (33) has been produced that exhibits cation recognition towards distinct cations.  $\text{Hg}^{2+}$  ions are strongly preferred by the ligand over other cations. The concurrent presence of  $\text{Hg}^{2+}$  ions was associated with an "OFF-ON" type of fluorescence activity. Furthermore, an ion-selective electrode (ISE) is created, and it exhibits superior selectivity for  $\text{Hg}^{2+}$  compared to all other tested cations. There is a  $7.08 \times 10^{-6} \text{ M}$  lower limit of detection (Fig. 18a) [52]. Fluorescent chemosensor hybrid material (34, Py-SBA-15) was synthesized to detect  $\text{Hg}^{2+}$  ions in water by functionalizing mesoporous silica (SBA-15) with a modified fluorescent chromophore, 1-(4-hydroxyphenyl)-4-pyrenyl-2,3-diaza-1,3-butadiene (Py-OH). The mesoporous hybrid material was prepared using Py-OH as the precursor, which was covalently bonded to the coupling agent 3-(triethoxysilyl)propylisocyanate (TESPIC). A mesoporous hybrid substance was prepared using Py-OH covalently bonded to 3-(triethoxysilyl)propylisocyanate

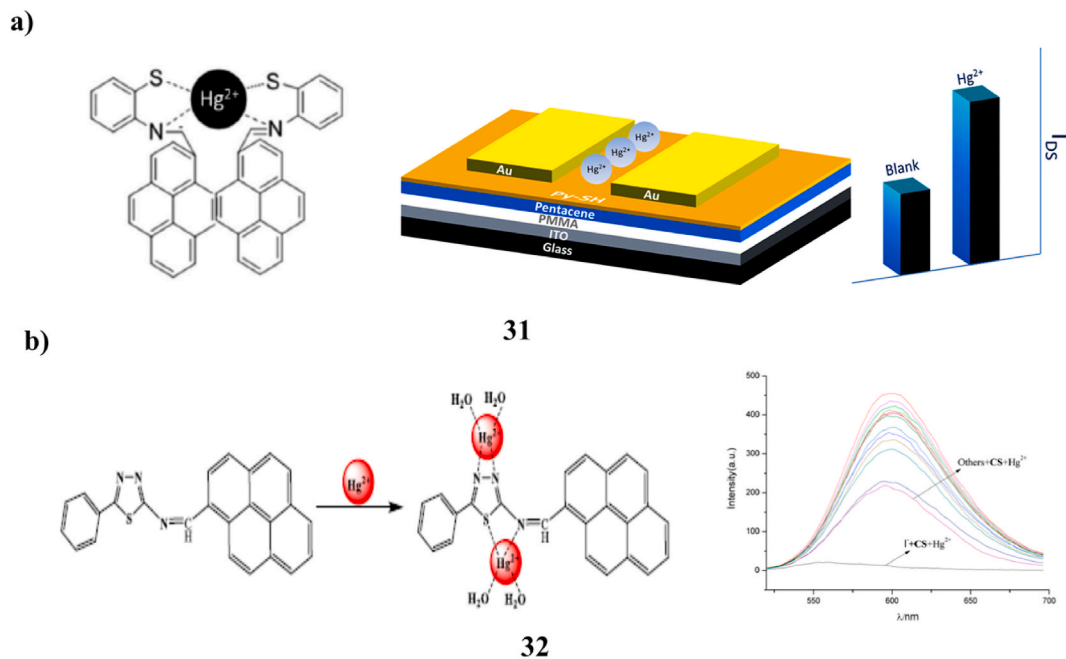


Fig. 17. a). Aquatic environments study of Pyrene-SH functionalized  $\text{Hg}^{2+}$  sensor (31). b). Photophysical study of pyrene  $\text{Hg}^{2+}$  Fluorescent Chemosensors (32).

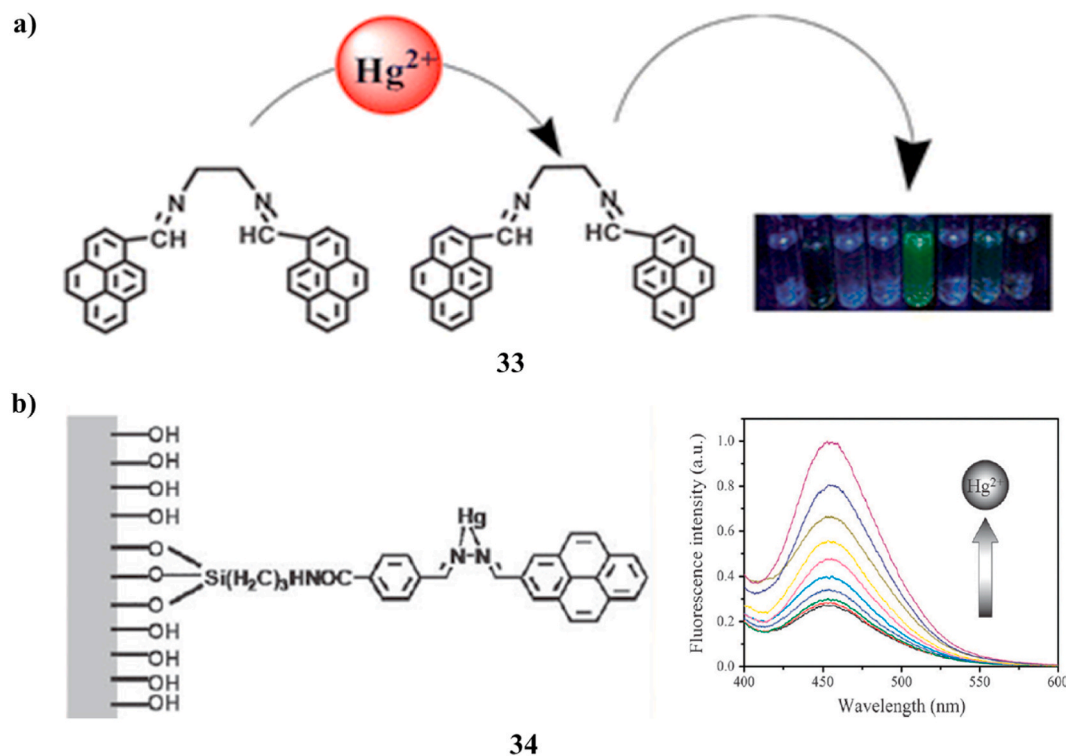


Fig. 18. a). Photograph of emission changes of bispyrenyl derivative mercury chemosensor (33). b). Py-SBA-15 sensor mechanism for  $\text{Hg}^{2+}$  ions (34).

(TESPIC) as a substrate. Py-SBA-15's XRD measurements and TEM pictures attest to the preservation of the hexagonally structured mesoporous structure following integration. Due to a significant increase in fluorescence caused by the incorporation of mercury ions during the suspension process of Py-SBA-15. In the presence of other metal ions, it displays a remarkable preference for  $\text{Hg}^{2+}$  ions. Py-SBA-15 fluorescence intensity and  $\text{Hg}^{2+}$  concentration in the solution are positively correlated ( $R^2 = 0.9989$ ) with a reasonable detection limit of  $1.7 \times 10^{-7} \text{ g mL}^{-1}$ . More notably, it has a strong regeneration ability because the covalent bonding technique significantly reduces the dissolution impact of the sensing molecules. According to the results of this research, this hybrid material has the possible to be a useful fluorescence chemosensor for identifying  $\text{Hg}^{2+}$  ions (Fig. 18b) [53].

The purpose of a ratiometric fluorescence sensor (35) was to identify biothiols in water and other biological materials, such as serum and urine. Biothiols affected the complexation-induced association and reaggregation of mercury ions and pyrene-thymine ions, which in turn regulated the variations in the monomer-excimer emission of the sensor (Fig. 19a). [54]. A new type of "turn on" fluorescent chemosensor based on pyrene (36), showed a significant increase in fluorescence intensity when  $\text{Hg}^{2+}$  ions were present and an exceptional selectivity towards  $\text{Hg}^{2+}$  ions throughout a wide range of metal ions in aqueous acetonitrile. It exhibits a 12-fold increase in fluorescence towards  $\text{Hg}^{2+}$  demonstrating its selectivity and sensitivity. The addition of  $\text{Hg}^{2+}$  ions to the probe caused an apparent color change that was discernible to the naked eye when exposed to UV light. Its *in vitro* sensitivity to  $\text{Hg}^{2+}$  in *candida albicans* cells was determined using confocal microscopy (Fig. 19b) [55].

A one-pot procedure was used to create the pyrene-based free thiol-containing Schiff base derivative (37). It is used in conjunction with live cell imaging as a fluorescence turn-on probe for  $\text{Hg}^{2+}$  ion detection. It demonstrated the fluorescence turn-on response to the presence of  $\text{Hg}^{2+}$  ions by excimer PT1-PT1\* production and chelation-enhanced fluorescence (CHEF). The sensing complex's 2:1 stoichiometry was determined using UV-Vis absorption titrations and the resultant plot. Furthermore, the sensor complex's binding locations were confirmed through the ESI-mass analysis, the fluorescence reversal of PT1+ $\text{Hg}^{2+}$  upon the addition of  $\text{Hg}^{2+}$  ions and EDTA, and the  $^1\text{H}$  NMR titrations. The concentrations of the  $\text{Hg}^{2+}$  complex's limit of detection (LOD) and association constant ( $K_a$ ) were determined using standard deviation and quadratic fits, as well as using the Benesi-Hildebrand 15 plot, accordingly. For the PT1+ $\text{Hg}^{2+}$  sensor system, additional investigations were conducted on the quantum yield ( $\Phi$ ), pH effect, time-resolved photoluminescence (TRPL) decay constant ( $\tau$ ) variations, and density functional theory (DFT). Crucially, the utility of PT1 as a fluorescent probe to detect  $\text{Hg}^{2+}$  in living cells was demonstrated by stereo fluorescence microscopy imaging in HeLa cells (Fig. 20a) [56]. A number of cyclotriphosphazene-based pyrene-functionalized chemosensors (38) with numerous binding sites were created and synthesized in a short amount of time using straightforward reaction methods, yielding excellent results. UV/Vis and fluorescence spectroscopies were used to examine their sensing behaviors towards  $\text{Hg}^{2+}$  ions. It showed clear selectivity and sensitivity at detection limits of up to 50 nM as being sufficient when compared to other existing techniques for the identification of mercury ions. A visible, proportional, and "TURN-ON" emission enhancement was apparent to the naked eye as a result of their combined effects of

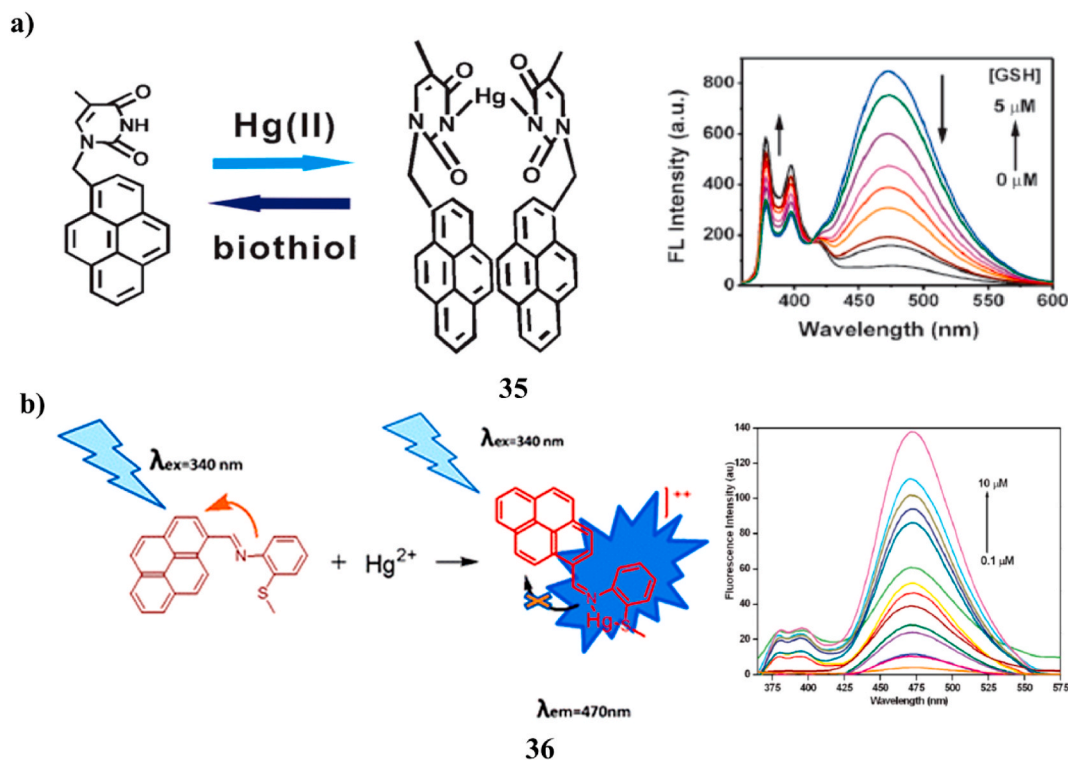


Fig. 19. a). Fluorescence studies of pyrene-biothiols based  $\text{Hg}^{2+}$  sensor (35). b). Confocal microscopy studies of pyrene-based  $\text{Hg}^{2+}$  chemo-sensor (36).

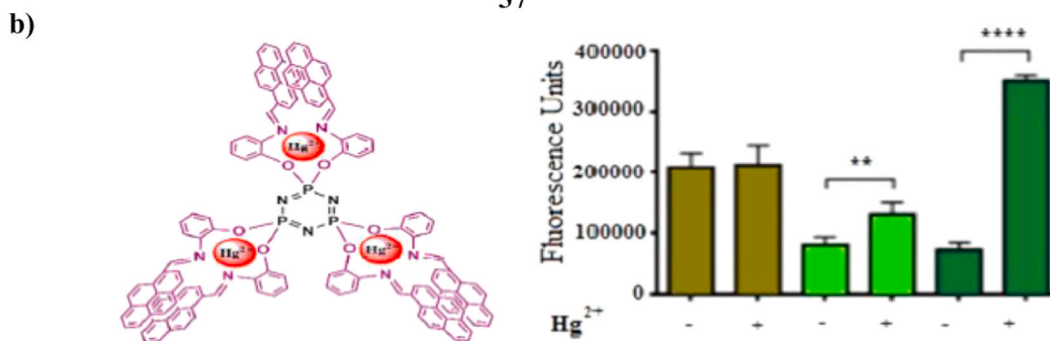
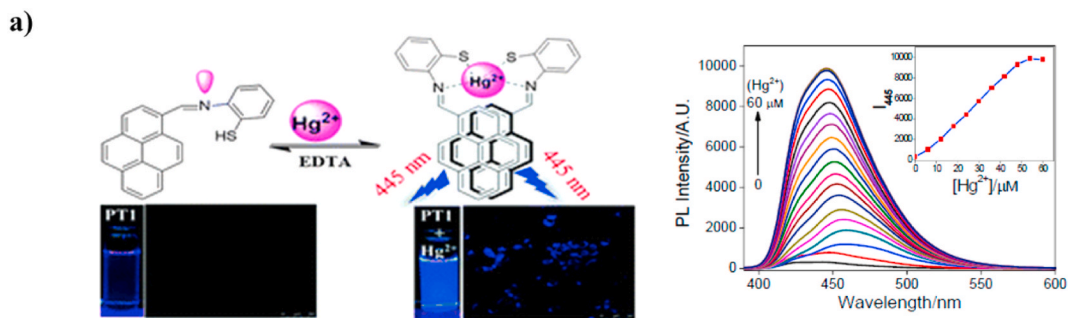


Fig. 20. a). Live cell application of Pyrene-based Schiff base probe fluorescent  $\text{Hg}^{2+}$  ions (37). b). Live cell imaging of pyrenyl-cyclotriphosphazenes based  $\text{Hg}(\text{II})$  chemosensors (38).

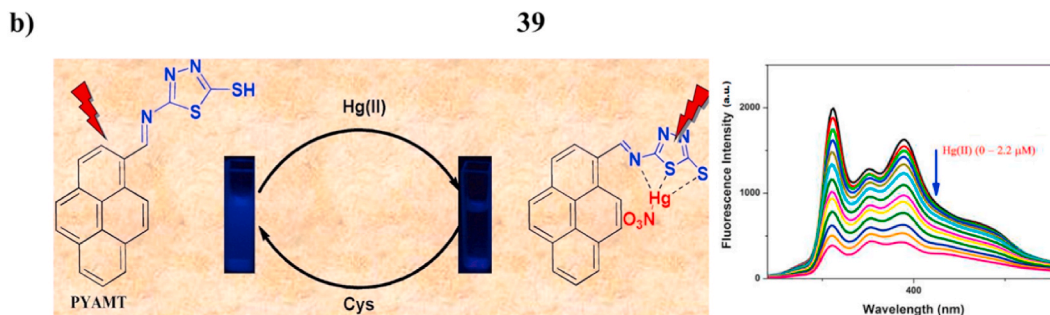
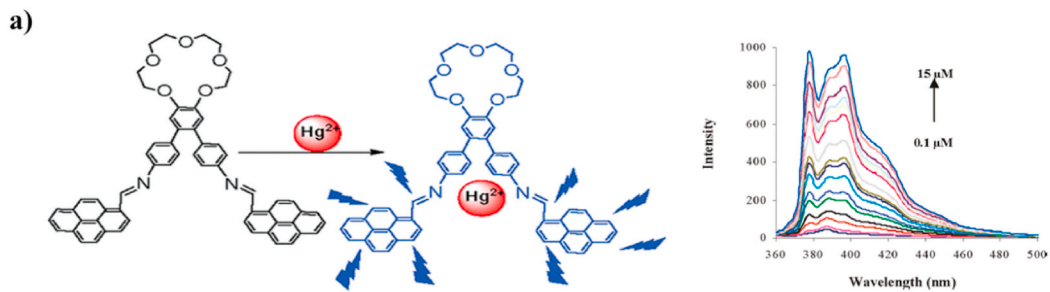


Fig. 21. a). Fluorescence response of Terphenyl derivatives of fluorescent sensors (39). b). Bioimaging studies of pyrene-amino mercaptothiadiazole based  $\text{Hg}^{2+}$  sensor (40).



chelation-enhanced fluorescence (CHEF), C=N isomerization, and intramolecular pyrene excimer formation due to the non-covalent  $\pi$ - $\pi$  and CH- $\pi$  stacking interactions. They can also be used to detect  $\text{Hg}^{2+}$  in live cells because they were shown to have no lethal effect on HeLa cancer cells. Comparing the  $\text{Hg}^{2+}$  sensing capabilities of chemosensors with three binding sites, it was shown that they were substantially more sensitive and capable of imaging mercury (II) than the comparable mono- and two-site ones. The findings show that molecular chemosensors growing ability to bind metal has increased their fluorescence detection sensitivity. This finding may be applied to different molecular systems to develop creative ways to boost chemosensor efficiency (Fig. 20b) [57].

UV-vis, fluorescence, and NMR spectroscopy have been used to develop, synthesize, and test new terphenyl-based reversible receptors (39) using pyrene and quinoline as the fluorophores for cation recognition towards different cations. The constructed receptors demonstrated the "Off-On" fluorescence signalling behavior for  $\text{Hg}^{2+}$  ions in THF and mixed aqueous environments, which is extremely sensitive and selective (Fig. 21a) [58]. A fluorogenic pyrene-amino mercaptothiadiazole (40, PYAMT) probe is used to determine  $\text{Hg}^{2+}$  in water samples with bioimaging applications in live cells. This method is very selective and sensitive. It showed three maxima of emission at 378, 388, and 397 nm ( $\lambda_{\text{ex}} = 348$  nm) and a trio of peaks of absorbance at 333, 348, and 394 nm. When 2.5  $\mu\text{M}$   $\text{Hg}^{2+}$  ion was added to  $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ , it exhibited strong fluorescent quenching (96%) with  $I/I_0 = 0.051$ , although its fluorescence did not change when other metal ions were present. The Heavy atom action of the  $\text{Hg}^{2+}$  ion followed by electron transfer is responsible for the quenching phenomena. With a threshold for detection of as few as 0.35 nM ( $S/N = 3$ ), the fluorescence intensity dropped linearly against an expansive range between 100 nM and 2.5  $\mu\text{M}$   $\text{Hg}^{2+}$  ( $R^2 = 0.9937$ ). PYAMT- $\text{Hg}^{2+}$  interaction equilibrium ratio is demonstrated to be 1:1 through DFT and fluorescence studies. For an OFF-ON process, the detector can detect cysteine reversibly which has a high association constant with the  $\text{Hg}^{2+}$  ion, approximately  $9.08 \times 10^5 \text{ M}^{-1}$ . Lastly, the suggested approach is effectively used to identify  $\text{Hg}^{2+}$  ions in real water samples and in bioimaging investigations involving living cells ((Fig. 21b) [59].

A new fluorescent probe made from pyrene-based products (41) having aggregation-induced emission (AIE) features was created. It was identified by NMR, SEM, UV-vis, fluorescence, and other methods. When compared to other metal ions in  $\text{H}_2\text{O}/\text{DMF}$  solvent, it showed great sensitivity and selectivity to  $\text{Hg}^{2+}$  with a detection limit of  $4.2 \times 10^{-7} \text{ M}$ . The probe-  $\text{Hg}^{2+}$  combination produced with a 2:1 synthesis having an additional dose of  $\text{Hg}^{2+}$ . Also, the probe showed high output of fluorescence and extremely minimal cytotoxicity in living cells. This demonstrated the probe's prospective applications for detecting  $\text{Hg}^{2+}$  in both environmental and living organisms (Fig. 22a) [60]. By post-functionalizing a macroporous polyacrylamide-based cryogel by adding a pyrene component a virtually recoverable fluorescent ion-sensing cryogel (42, PAAm-Pyr) was created. The sensor has remarkable selectivity for  $\text{Hg}^{2+}$  even in the presence of opposing metal ions in water that is purified, while it can detect  $\text{Hg}^{2+}$  concentrations as low as 2 ppb in aqueous solutions. The created sensor may be cleaned with pure water and used repeatedly (Fig. 22b) [61].

Fluorescence quenching was observed in three novel pyrene derivatives (43) that included two triazole units when exposed to  $\text{Hg}^{2+}$

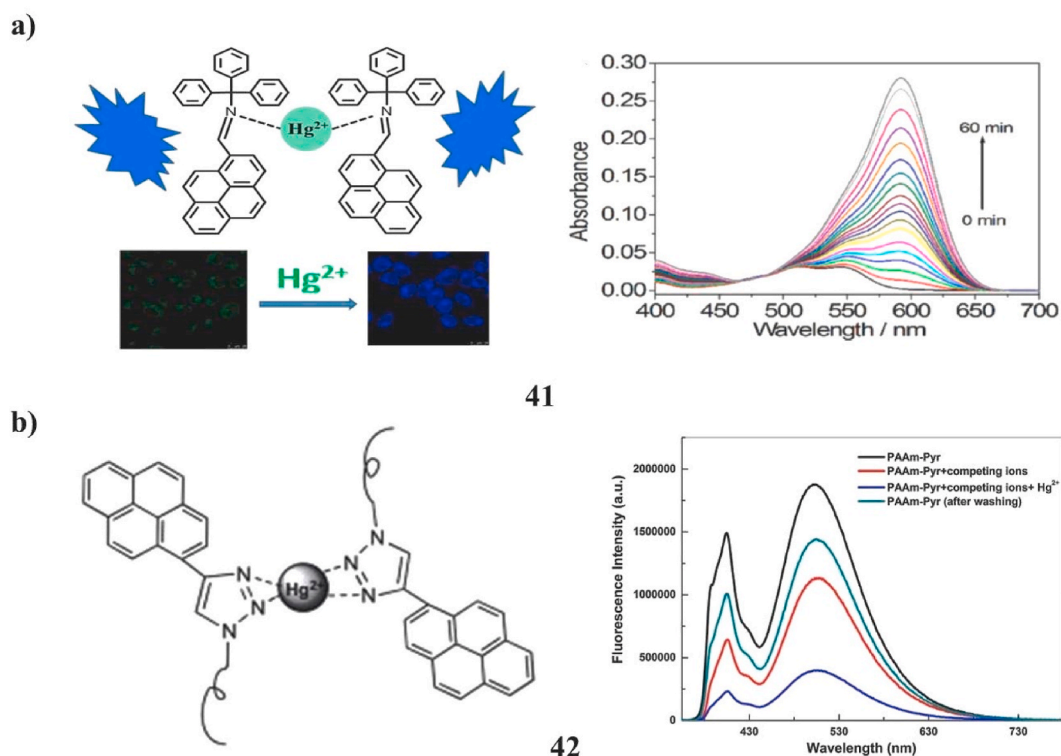
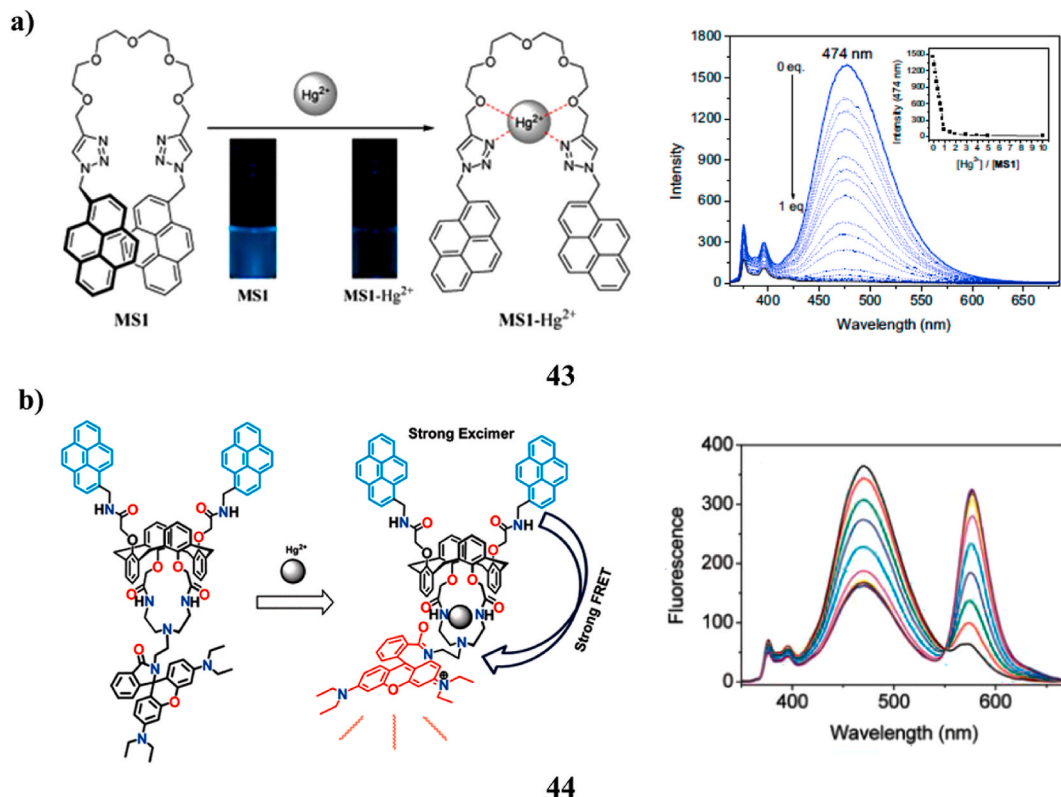


Fig. 22. a). AIE study of pyrene-based  $\text{Hg}^{2+}$  fluorescent probe (41). b). Fluorescence Quenching of Pyrene-Polyacrylamide-Based Mercury (II) Sensor (42).

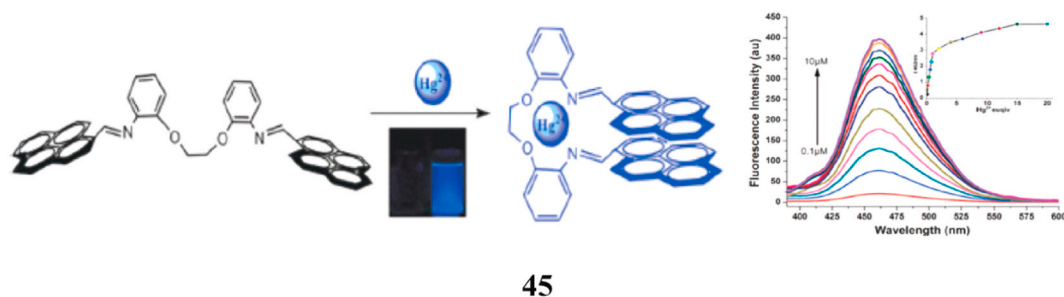


**Fig. 23.** a). Fluorescence study of pyrene-triazole based fluorescent sensors (43). b). FRET study of Pyrene Excimer-Based Calix arene Chemosensor (44).

ions. It was discovered that the chemosensor- $\text{Hg}^{2+}$  combinations had attachment constants ( $K_a$ ) of  $1.68 \times 10^3 \text{ M}^{-1}$ ,  $1.57 \times 10^3 \text{ M}^{-1}$ , and  $1.52 \times 10^3 \text{ M}^{-1}$  in that order. Additionally, studies using fluorescence microscopy demonstrated the efficacy of a fluorescent probe in identifying  $\text{Hg}^{2+}$  within live cells (Fig. 23a) [62]. A new calixarene derivative (44) with two pyrene and rhodamine fluorophores bound in the 1,3-alternate conformation was created as a  $\text{Hg}^{2+}$  ion-selective sensor. The sensor depends on FRET coupling ring-opened rhodamine absorbance following the association of the  $\text{Hg}^{2+}$  ion to pyrene excimer emissions. By using FRET with an excitation at 343 nm, adding a bit of  $\text{Hg}^{2+}$  to a combined solution of sensor resulted in noticeably increased fluorescence at about 576 nm. They discovered that intramolecular  $\pi$ - $\pi$  interactions produce stronger FRET bands than between molecules  $\pi$ - $\pi$  interactions (Fig. 23b) [63].

A new pyrene derivative with an azadiene group was developed as a ratiometric chemosensor (45) for mercury in a solution of aqueous acetonitrile. The fluoroionophores "OFF-ON" type signalling behavior is caused by conformational changes brought on by metal ions, which increase the emission of strong pyrene excimer from weak pyrene monomer (Fig. 24) [64].

Pyrene-based mercury (II) sensors utilize the unique photophysical properties of pyrene, which exhibit significant fluorescence changes upon interaction with mercury ions. The sensing mechanism often involves the quenching of pyrene fluorescence due to the formation of a complex between pyrene derivatives and mercury ions. This interaction results in a measurable reduction in fluorescence intensity, enabling sensitive detection. Advantages include high sensitivity, selectivity, and potential for real-time monitoring. Limitations involve photobleaching and environmental stability. In practical applications, such sensors are integrated into IoT and



**Fig. 24.** Ratiometric study of Azadiene-Pyrene based  $\text{Hg}^{2+}$  Chemosensor (45).

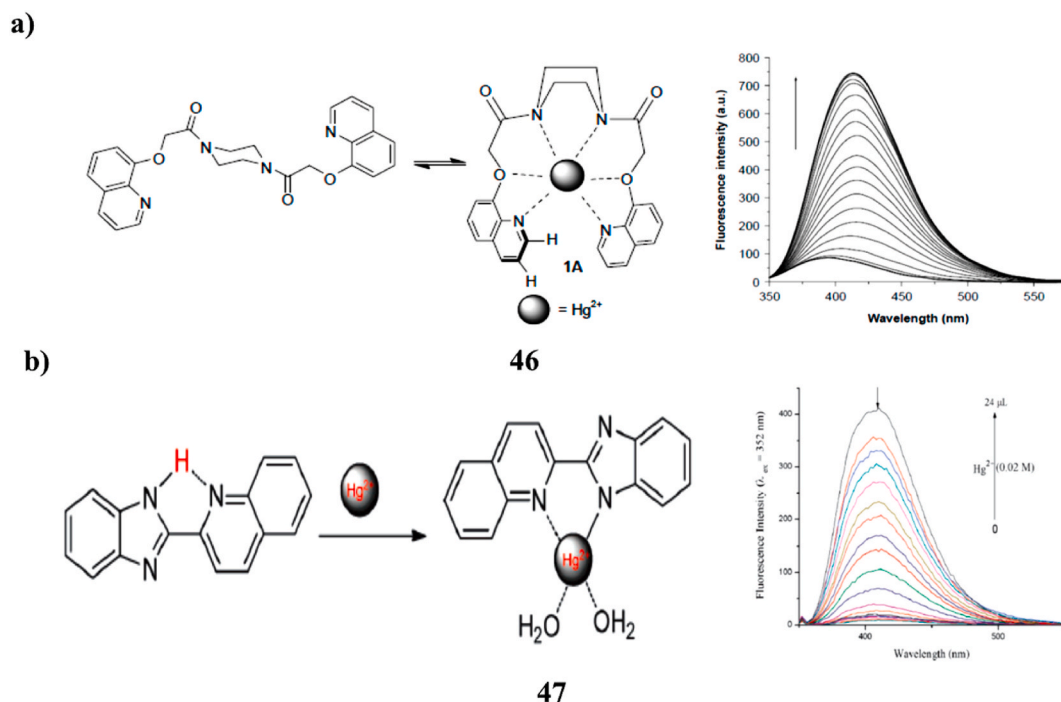
wearable devices for environmental monitoring and health diagnostics. For instance, pyrene-based sensors have been deployed in wearable devices for detecting mercury contamination in water and air, demonstrating their effectiveness in real-world scenarios.

## 6. Quinoline based mercury ( $\text{Hg}^{2+}$ ) sensor

A novel quinoline-based chemosensor (**46**) has been created and produced. Its ability to bind metal ions has been shown in both aqueous and organic solutions. However, chemosensors identify  $\text{Hg}^{2+}$  ions ( $K_a = 2.15 \times 10^4 \text{ M}^{-1}$ ) by displaying a ratiometric shift in  $\text{CHCl}_3/\text{CH}_3\text{OH}$  emission. In comparison with the other metal ions analyzed, it demonstrates a higher selectivity for  $\text{Hg}^{2+}$  ions ( $K_a = 9.20 \times 10^3 \text{ M}^{-1}$ ) (Fig. 25a) [65]. A new non-sulfur mercury fluorescent chemosensor (**47**) has been devised and manufactured. It uses the quinoline and benzimidazole groups as the fluorescence signal groups. Fluorescence spectroscopic variations in the  $\text{H}_2\text{O}/\text{DMSO}$  solution allowed the binding site to recognize the  $\text{Hg}^{2+}$  cation with excellent sensitivity as well as specificity. The fluorescence colors of the solution-containing sensor changed dramatically from blue to colorless shortly after  $\text{Hg}^{2+}$  was added to the aqueous media, whereas other cations did not cause significant color changes. Further investigation further shows that the sensor's detection limit for the fluorescence response to  $\text{Hg}^{2+}$  is  $9.56 \times 10^{-9} \text{ M}$ , well below the EPA's allowable amount of mercury in drinking water of 0.01 M. Ligand-based test strips were created to serve as practical and effective  $\text{Hg}^{2+}$  test kits. Therefore, the probe should be useful for detecting mercury in an aquatic environment (Fig. 25b) [66].

Synthesis and characterization of a water-soluble fluorescence sensor based on 2-(2-(8-hydroxyquinolin-yl)benzimidazole) (**48**) have been completed. In buffered aqueous solution, it exhibits extremely selective and sensitive detection of  $\text{Hg}^{2+}$  with a fluorescence "ON-OFF" response. The nitrogen and oxygen molecules of 8-hydroxyquinoline and the imine N atom of the benzimidazole unit bind  $\text{Hg}^{2+}$  through a 1:1 binding stoichiometry, according to the X-ray structural analysis of the  $\text{Hg}^{2+}$  complex. Quantum chemistry analyses qualitatively examine the workings of stopping fluorescence and demonstrate that ligand-to-metal charge transfer (LMCT) in the state of excitation is the origin of the phenomena (Fig. 26a) [67]. The purpose of this study was to design and synthesize a new phenothiazine-based derivative (**49**). As a result of the development of a 1:1 metal-ligand complex, this molecule showed considerable fluorescence quenching following the introduction of  $\text{Hg}^{2+}$ . Its exceptional sensitivity towards Hg (II) was accompanied by a fast reaction time and a good selectivity for  $\text{Hg}^{2+}$  over other transition metal ions. Concurrently, the experiment on cell imaging showcased the significance of the sensor in fluorescently seeing  $\text{Hg}^{2+}$  within biological systems (Fig. 26b) [68].

A chemosensor derived from benzothiazoles (**50**) has been developed by using the excited state proton transfer (ESIPT) mechanism. It differentiates  $\text{Hg}^{2+}$  from a range of physiologically significant metal ions and hazardous heavy metal ions by causing a fluorescence turn-on response only in the presence of  $\text{Hg}^{2+}$  ions. With a detection limit as low as 0.11  $\mu\text{M}$ , it demonstrates excellent sensitivity. Calculations based on theories employing the theory of density functions, ESI-MS spectral analyses, and  $^1\text{H}$  NMR titrations all indicate the metal binding. In HeLa cells, it displays the permeability and effectiveness of their cell membrane for  $\text{Hg}^{2+}$  detections (Fig. 27a) [69]. A new colorimetric and fluorescent "ON-OFF" chemosensor **10** (**51**) based on a photochromic diarylethene with a quinoline unit



**Fig. 25.** a). Ratiometric sensing of quinoline-based  $\text{Hg}^{2+}$  chemosensor (**46**). b). Fluorescence spectra of benzimidazole-quinoline based  $\text{Hg}^{2+}$  chemosensor (**47**).

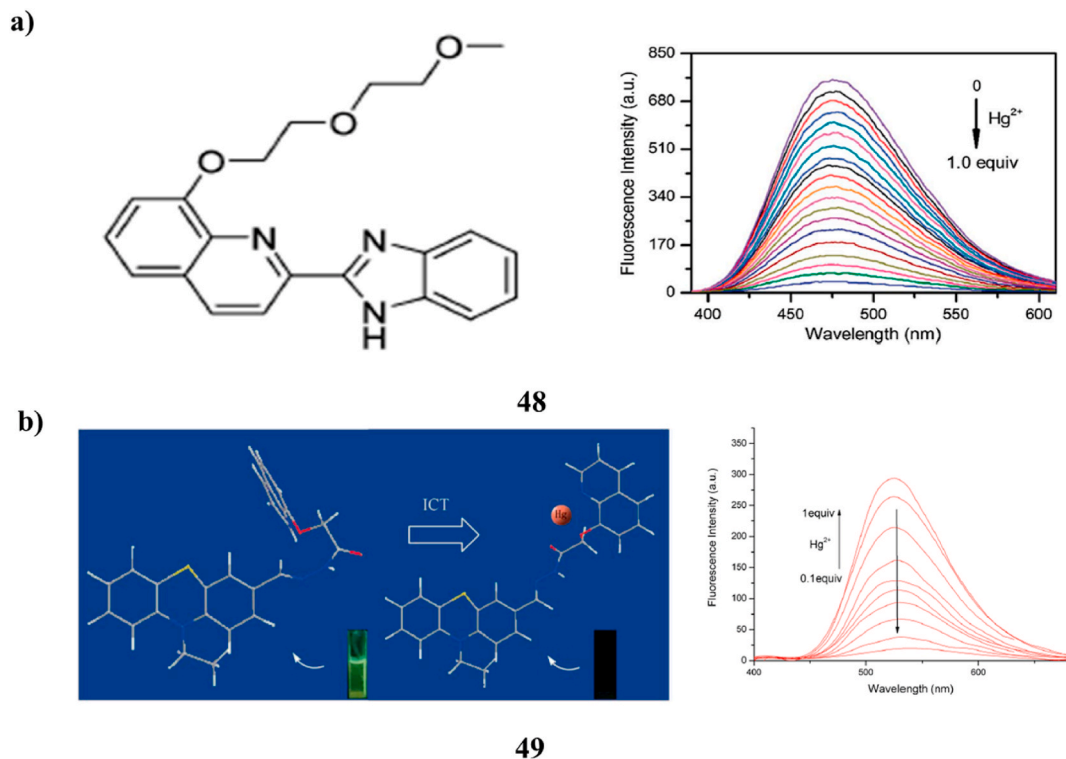


Fig. 26. a). Ligand-to-metal charge transfer study of quinoline-benzimidazole based  $\text{Hg}^{2+}$  fluorescent sensor (48). b). Living cells study of phenothiazine-based fluorescent sensor (49).

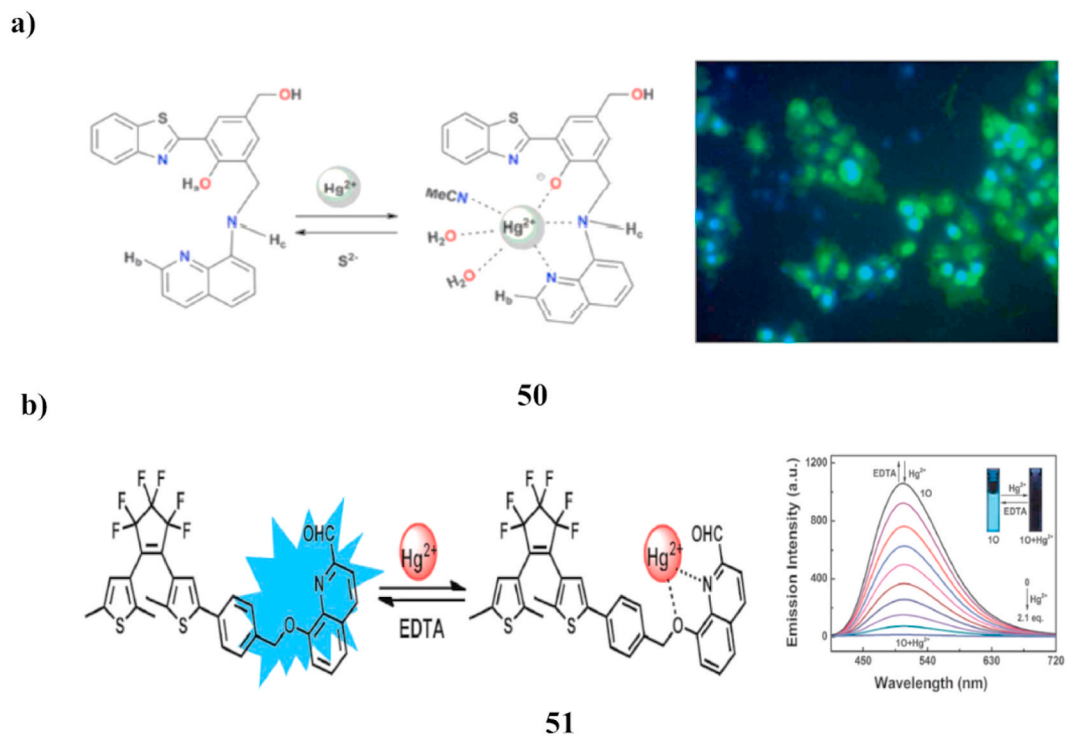


Fig. 27. a). ESIPT study of HBT-quinoline conjugate-based  $\text{Hg}^{2+}$  sensor (50). b). Emission spectra of diarylethene-quinoline based chemosensor (51).

was developed and synthesized. In acetonitrile, the chemosensor 1O showed sensitivity and selective  $\text{Hg}^{2+}$  ion detection even in an atmosphere of competing metal ions. The detector 1O's stoichiometric ratio for  $\text{Hg}^{2+}$  was found to be 1:1, and the probe 1O's detection limit for  $\text{Hg}^{2+}$  was computed to be 56.3 nM. Additionally, a molecular logic circuit exhibiting metal-responsive behavior and UV/vis light-responsiveness was successfully built with 4 inputs along with one output. The binding behavior between 1O and  $\text{Hg}^{2+}$  is confirmed by  $^1\text{H}$  NMR titration tests, Job's plot analysis, and ESI-MS spectroscopy (Fig. 27b) [70].

A new quinoline-based ratiometric fluorescence probe (52) known as the "naked-eye" was developed. The  $\text{Hg}^{2+}$  ion-containing probe has a 2:1 reactive stoichiometry. With a 410-fold rise in absorbance concentration ratio ( $A_{402}/A_{340}$ ) in the presence of water throughout a wide pH value range, it demonstrated a high degree of selectivity towards  $\text{Hg}^{2+}$  ions compared to other metal ions. It also showed a resonant shifting of color from colorless to pale yellow that was noticeable to the naked eye (Fig. 28a) [71]. The click method has been used to create a number of innovative C-glycosyl triazolyl quinoline-based fluorescence sensors (53). It was discovered that new sensors have strong  $\text{Hg}^{2+}$  selectivity over a wide range of other metal ions as well. In order to improve the fluorescent sensors' water-soluble properties and expand their range of applications for  $\text{Hg}(\text{II})$  detection in biological structures with water solubility, the glucose structure was introduced. Several spectroscopic approaches have been used to characterize the binding mode of triazolyl quinoline with  $\text{Hg}^{2+}$ , which has been identified as the mechanism behind the sensors' chemodosimetric behaviour (Fig. 28b) [72].

A new Schiff base probe (54, QT) containing thiophene-2-carboxaldehyde (T) and 8-aminoquinoline (Q) moieties has been synthesized. When QT becomes exposed to  $\text{Hg}^{2+}$ , chelation enhances its fluorescence quenching because the nitrogen and sulfur atoms of QT coordinate, making QT an easy "turn-off" sensor. UV-visible absorption and emission spectral studies,  $^1\text{H}$  NMR titration, and calculation using density functional theory all supported the development of the chelation complex. According to these investigations, the probe shows excellent sensitivity and selectivity towards  $\text{Hg}^{2+}$  when other common metal ions are present. The low detection limit of 23.4 nM was established, and a 2:1 stoichiometry between QT and  $\text{Hg}^{2+}$  was verified by a job plot. Moreover, confocal fluorescence microscopy was used to assess the potential usefulness of QT as a sensor for  $\text{Hg}^{2+}$  ions in human HeLa cells, and Whatman filter paper strips were used to evaluate the sensor's appropriateness for field application using environmental samples (Fig. 29) [73].

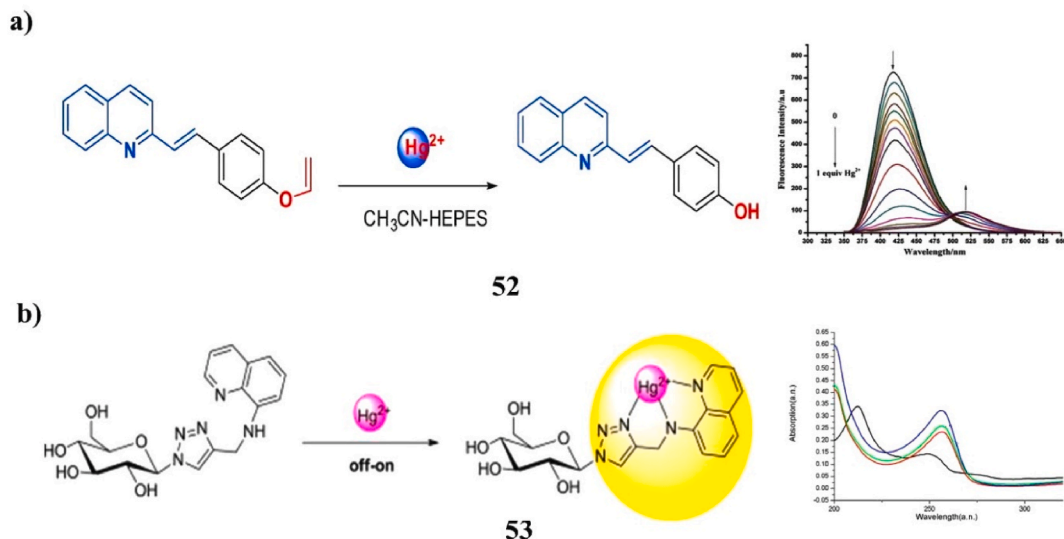
Quinoline-based mercury (II) sensors utilize a fluorescence quenching mechanism for mercury detection, where the binding of mercury ions to the quinoline moiety alters its photophysical properties, resulting in a measurable decrease in fluorescence intensity. This high sensitivity to mercury ions is advantageous for trace detection. Quinoline sensors offer benefits such as high selectivity, low detection limits, and potential for integration into IoT and wearable devices due to their compact size and efficient sensing capabilities. However, limitations include potential interference from other metal ions and stability issues. Real-world applications include environmental monitoring and health diagnostics, as demonstrated by their use in wearable devices for detecting mercury exposure in occupational settings.

## 7. Rhodamine based mercury ( $\text{Hg}^{2+}$ ) sensors

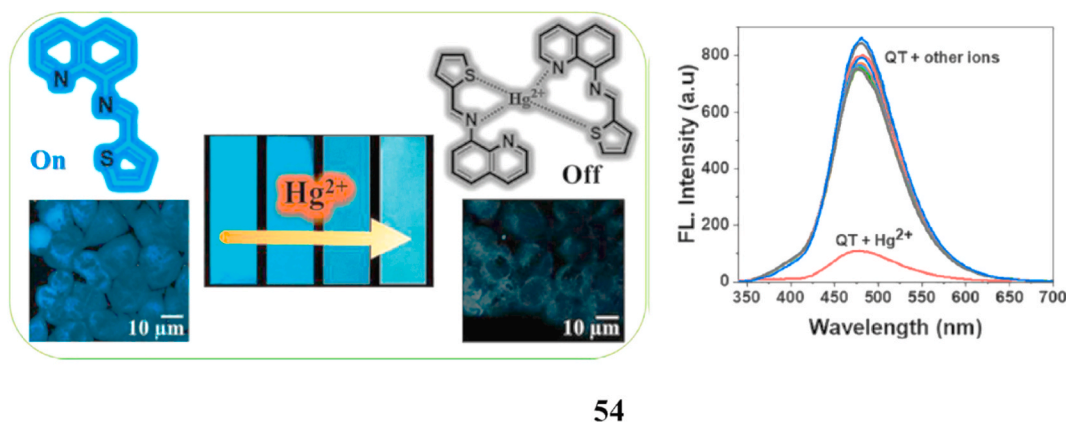
A new rhodamine hydrazone derivative (55) featuring thiol and carboxylic acid groups is developed as a selective fluorescent and colorimetric chemosensor for  $\text{Hg}^{2+}$ . The substantial fluorescence amplification and colorimetric transformation upon the addition of  $\text{Hg}^{2+}$  are made possible by the ring-opening mechanism of spirolactam. Confocal laser scanning microscopy was used to analyze one of the chemosensors in a microchannel after it had been combined with an object containing  $\text{Hg}^{2+}$ . The fluorescence brightness of both chemosensors showed a linear response ( $r^2 = \mu 0.95$ ) in the range of 1 nM when plotted against the log concentration of  $\text{Hg}^{2+}$ , the corresponding detection limits were 1 nM and 4.2 nM (Fig. 30a) [74]. Rhodamine B was combined with the 8-hydroxyquinoline group to provide a unique fluorescent probe (56). The results demonstrated highly responsive and specific fluorescence emission above 500 nm and  $\text{Hg}^{2+}$  amplified absorbance in an aqueous solution with a broad pH range of 4–9. The finding that mercury ions align reversibly to the opening spirolactam ring led to the formation of a 1:1 metal-ligand complex. It was also used to confirm its usefulness as a fluorescent probe for monitoring  $\text{Hg}^{2+}$  in living cells using in vivo imaging in HeLa cells (Fig. 30b) [75].

A rhodamine-based novel and highly sensitive colorimetric off-on fluorescent chemosensor (57) for  $\text{Hg}^{2+}$  ions is formulated and synthesized, utilizing the renowned thiospirolactam rhodamine chromophore and furfural hydrazone as signal-reporting groups. Investigated are the sensor's  $\text{Hg}^{2+}$ -binding characteristics and photophysical characterization in a neutral DMF aqueous solution. A specific metal ion-induced reversible ring-opening mechanism of the rhodamine spirolactam is required for the chemosensor signal to change. The chemosensor reacts instantly and reversibly to  $\text{Hg}^{2+}$  ions. Compared with other metal ions, it effectively displays a significant "turn-on" reaction toward  $\text{Hg}^{2+}$ . Further proving the sensor's usefulness for real-world applications in biological and environmental structures, it is also employed for in vivo imaging in Rat Schwann cells to verify that the probe may be used as a fluorescent probe for monitoring  $\text{Hg}^{2+}$  in living cells with satisfactory results (Fig. 31a) [76]. The design and description of a fluorescent turn-on chemosensor (58, RN2) for  $\text{Hg}^{2+}$  based on rhodamine B thiohydrazide was done. It demonstrated exceptionally high selectivity and sensitivity to  $\text{Hg}^{2+}$  in comparison to other metal ions. The  $\text{Hg}^{2+}$ -induced breaking of the spiro ring in rhodamine B resulted in selective "OFF-ON" type fluorescence amplification and a noticeable color shift in the RN2. Biological imaging experiments showed the said probe was fluorescent and able to be employed as a cell-permeable probe for  $\text{Hg}^{2+}$  monitoring in living cells. It was also effective to use the constructed chemosensor to identify  $\text{Hg}^{2+}$  in water samples obtained from the environment (Fig. 31b) [77].

Rapid colorimetric and fluorometric sensing is demonstrated by a rhodamine-based sensor (59) with dual ion detection features following 1:1 binding with  $\text{Hg}^{2+}$ . The  $\text{Hg}^{2+}$ -induced opening of the spirolactam ring in the rhodamine structure is responsible for the solution's apparent color shift from colorless to pink and the fluorescence color shift from dark to orange. Fluorescence methods yielded a detection limit of 44 nM, whereas absorbance yielded a value of 32 nM. Moreover, the resultant complex  $\text{Hg}^{2+}$  may be used as an  $\text{I}^-$  reversible flux sensor. The addition of  $\text{I}^-$  strengthened the force that links  $\text{Hg}^{2+}$  and  $\text{I}^-$  by grabbing the  $\text{Hg}^{2+}$  in the complex, which decreased the amount of fluorescence. A molecular device based on the "OFF-ON-OFF" characteristic was constructed with a



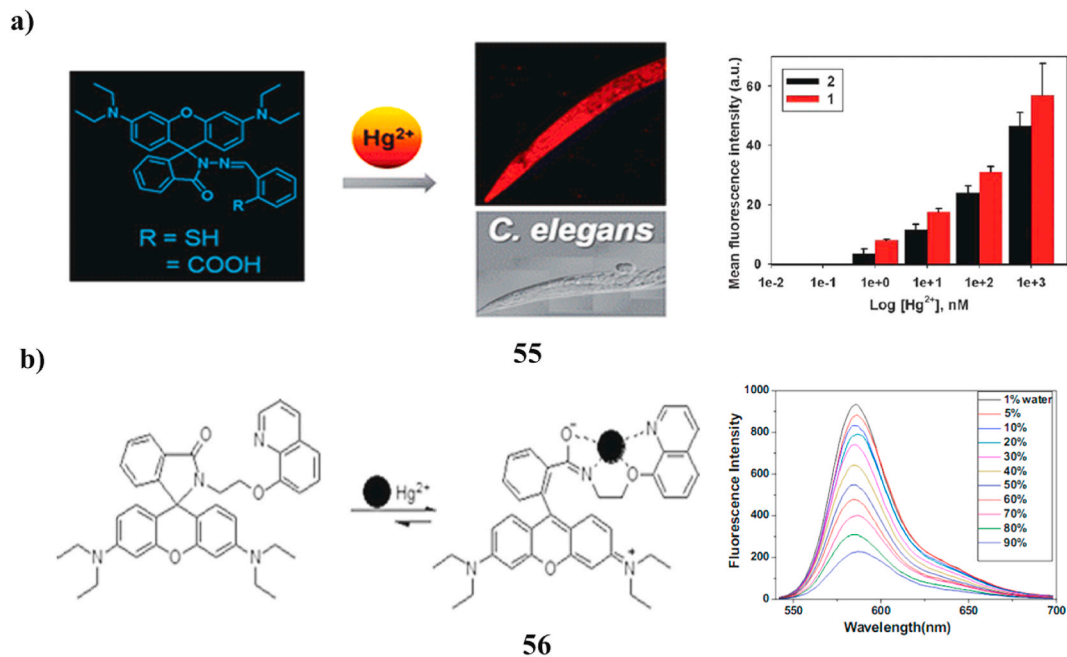
**Fig. 28.** a). Fluorescence titration of Naked-eye' quinoline-based 'reactive'  $\text{Hg}^{2+}$  sensor (52). b). UV-Vis spectra of C-glycosyl triazolyl quinoline-based fluorescent sensors (53).



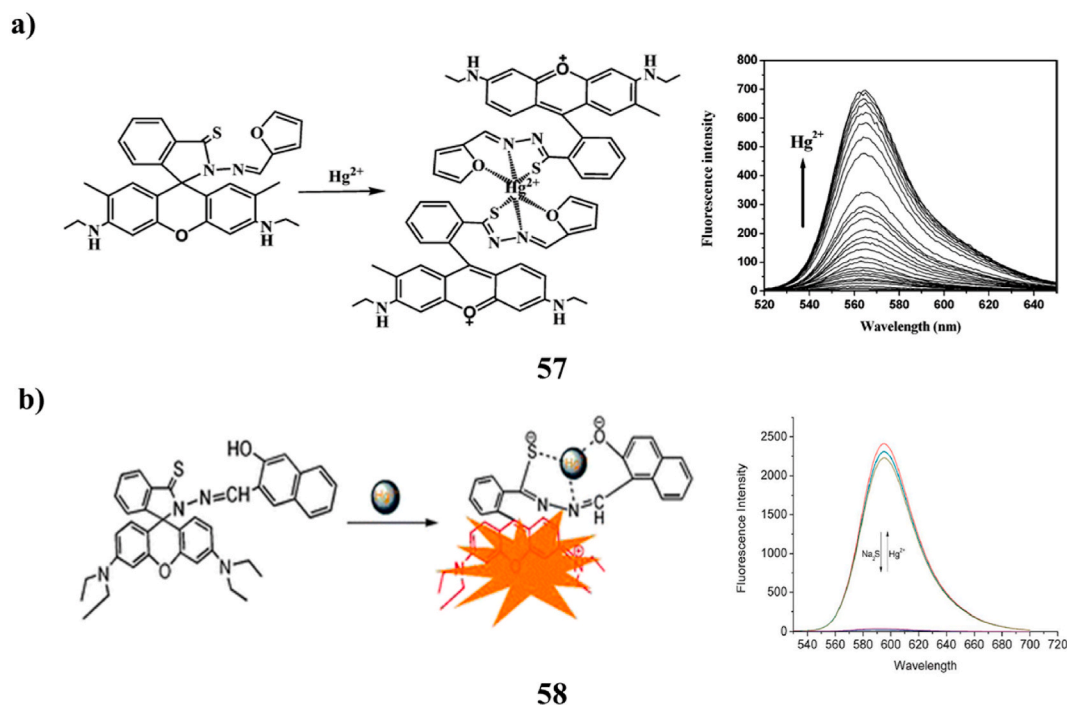
**Fig. 29.** Confocal fluorescence study of quinoline-thiophene based chemosensor (54).

"INHIBIT" logic gate function (Fig. 32a) [78]. A chemosensor (60) using rhodamine-B and diphenylselenium (RhoSe) has been created. UV/Vis and fluorescence spectroscopy have been used to study its reaction to different metal ions. In  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  solutions, it responds to  $\text{Hg}^{2+}$  more so than other metal ions. The RhoSe solution exhibits a noticeable color shift from colorless to pink upon the addition of  $\text{Hg}^{2+}$ , as well as a notable 48-fold increase in fluorescence. Caused by  $\text{Hg}^{2+}$  binding, the ring-opening of the spiro-lactam in the rhodamine fluorophore is responsible for the color shift and increased fluorescence. The binding ratio of  $\text{RhoSe}-\text{Hg}^{2+}$  was determined using a work plot, and it was discovered to be 1:1. The pH range of 4.0–10 proved the most effective for  $\text{Hg}^{2+}$  detection. Significantly, the inclusion of  $\text{Na}_2\text{S}$  allowed for the observation of the  $\text{RhoSe}-\text{Hg}^{2+}$  complex's reversibility. For practical purposes, the  $\text{Hg}^{2+}$  in a water/methanol solution was detected using the strip technique. Furthermore, confocal fluorescence microscopy shows that RhoSe is a useful fluorescent probe for  $\text{Hg}^{2+}$  detection *in vitro* and *in vivo* (Fig. 32b) [79].

Rhodamine 6G served as the basis for the design, synthesis, and characterization of a fluorescent and colorimetric chemosensor (61). It successfully identified  $\text{Hg}^{2+}$  based on a two-step reaction. Through the use of Fourier-transform infrared spectroscopy, electrospray ionization-mass spectrometry, ultraviolet-visible spectrophotometry, fluorescence spectroscopy, and frontier molecule orbital simulations, the interaction between the chemosensor and  $\text{Hg}^{2+}$  was verified. Additionally, it was added to silica gel plates and test strips, which showed excellent  $\text{Hg}^{2+}$  selectivity and sensitivity (Fig. 33a) [80]. Three brand-new  $\text{Hg}^{2+}$  fluorescence sensors (62) based on rhodamine were created and manufactured. It exhibited exceptional fluorescence amplification and demonstrated good selectivity and sensitivity to  $\text{Hg}^{2+}$  even in semi-aqueous solutions with a pH close to neutral. The thiourea-unit numbers rose for these three sensors, expanding their linear operating range and raising their sensitivity. Additionally, the sensors demonstrated outstanding resistance to interference from several metal ions that are relevant to both the environment and biology. The sensors' good practicality was demonstrated by the pond and tap water test. A novel mechanism of interaction between  $\text{Hg}^{2+}$  and the sensor was



**Fig. 30.** a). Microfluidic system of Rhodamine-hydrazone based  $\text{Hg}^{2+}$  chemosensors (55). b). Live cell imaging study of Rhodamine-hydroxyquinoline based  $\text{Hg}^{2+}$  chemosensor (56).



**Fig. 31.** a). Live cell imaging of Rho6G-thispirolactam based chemosensor (57). b). Bioimaging study of RhB thiohydrazone based  $\text{Hg}^{2+}$  chemosensor (58).

suggested by the number of bound  $\text{Hg}^{2+}$  matching that of the thiourea units and the irreversible recognition process (Fig. 33b) [81].

The high selectivity for  $\text{Hg}^{2+}$  detection was achieved by designing and synthesizing the rhodamine-based fluorescent chemosensor (63). Characterization was conducted through IR,  $^1\text{H}$  NMR, and HRMS spectroscopies. In an ethanol/water solution, it demonstrated clear fluorescence and colorimetric shifts toward  $\text{Hg}^{2+}$ , which led to the formation of  $\text{Hg}^{2+}$  complex with the  $\text{Hg}^{2+}$ -induced ring opening

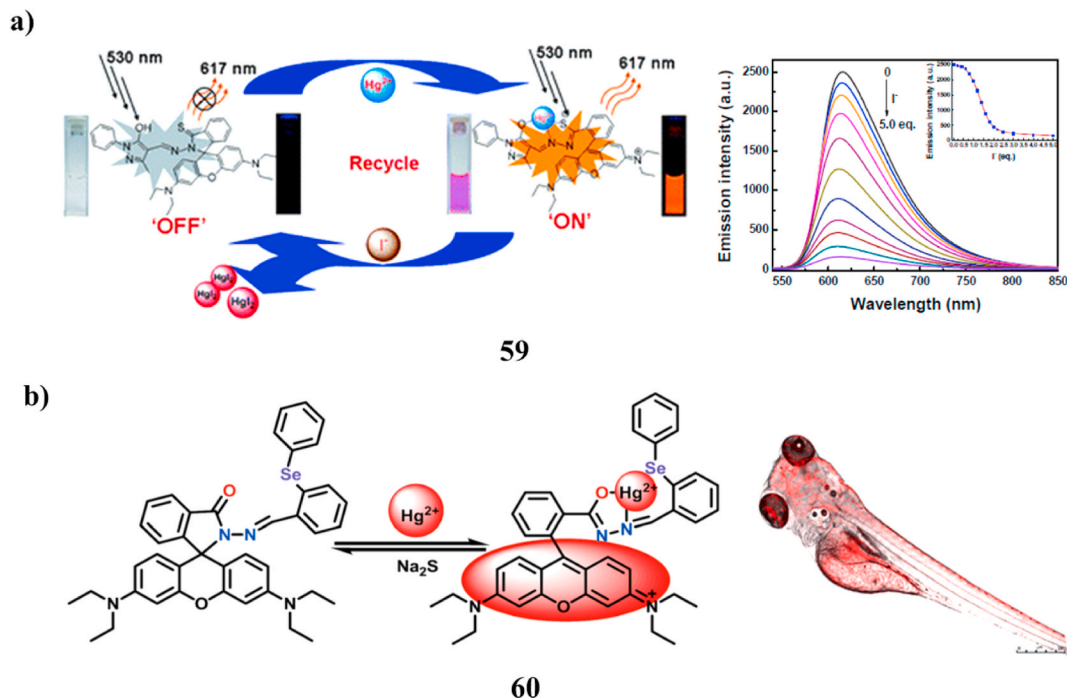


Fig. 32. a). Fluorescence analysis of a  $\text{Hg}^{2+}$  sensor based on rhodamine B (59). b). Zebrafish study of RhoSe-based chemosensor (60).

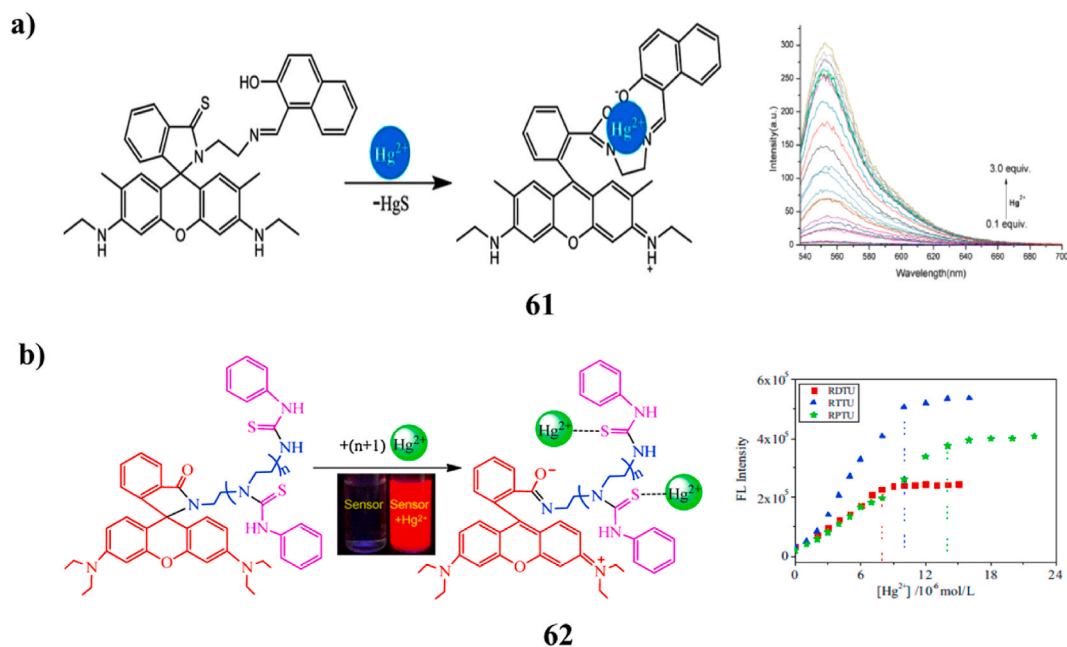
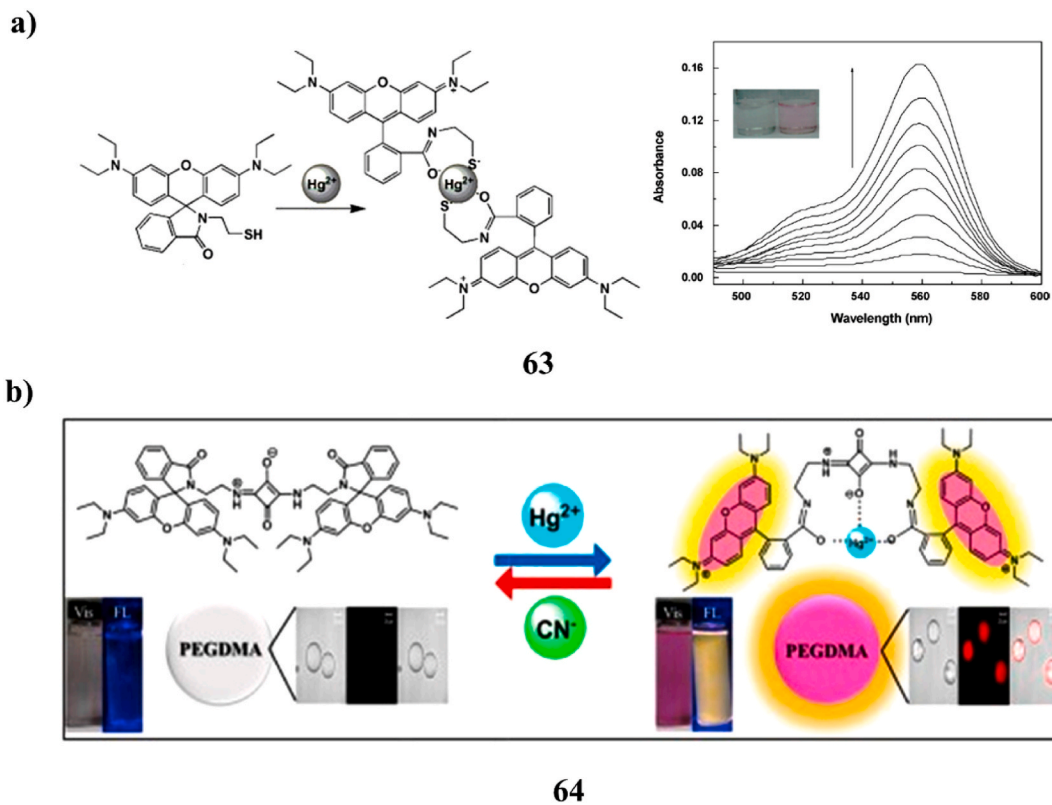


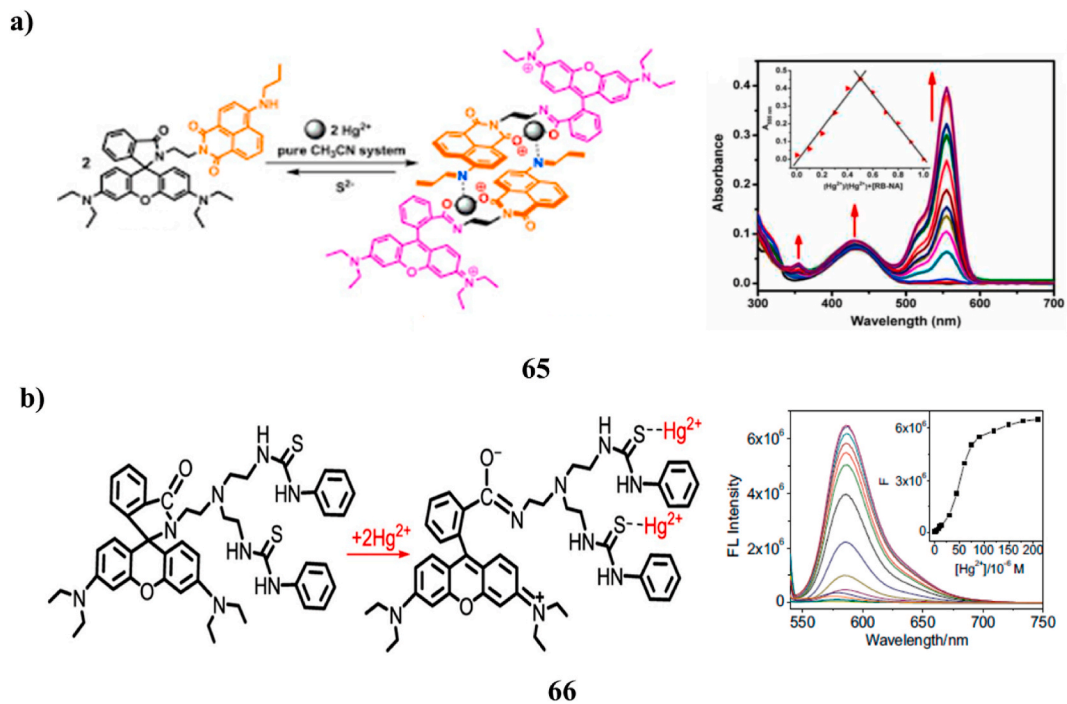
Fig. 33. a). Fluorescent study of Rho6G-based  $\text{Hg}^{2+}$  Chemosensor (61). b). FL intensity of RhB thiourea-based fluorescent sensors (62).

of the spirolactam ring in rhodamine. By its spectral response with  $\text{Hg}^{2+}$  ions as well as TBAI (tetrabutylammonium iodide) titration studies, the chemosensor's reversibility was confirmed (Fig. 34a) [82]. A rhodamine B group linkage introduced as a reversible switch into squaraine-diamine dyads is an efficient method based on coordination-induced signalling. A new optical squaraine-bis (rhodamine-B) chemosensor (64, SRB) was designed and synthesized, and its best possible usage was investigated. The goal of the probe was to identify  $\text{Hg}^{2+}$  ions using an "OFF-ON" fluorescence system. In the presence of other metal ions, it demonstrated a high selectivity toward  $\text{Hg}^{2+}$ . The complex known as SRB- $\text{Hg}^{2+}$  was studied through the use of UV-vis and fluorescence spectroscopy in





**Fig. 34.** a). Absorption properties of RhB-based  $\text{Hg}^{2+}$  chemosensor (63). b). Cell imaging study of squaraine-bis(rhodamine-B) based chemo-sensor (64).



**Fig. 35.** a). UV study of Naphthalimide-Rhodamine based  $\text{Hg}^{2+}$  chemosensors (65). b). Living cell study of RhB-thiol based  $\text{Hg}^{2+}$  fluorescent sensor (66).

acetonitrile since it demonstrated a high degree of selectivity towards  $\text{Hg}^{2+}$  when exposed to different metal ions. The probe's "OFF-ON" fluorescence and color signal shift are due to a domino effect triggered by  $\text{Hg}^{2+}$ , which uses rhodamine spirolactam in its open-ring form to restore the conjugated mechanism of the rhodamine skeleton. Employing a job plot calculation, optical titration, and FT-IR, the mechanism for the opening of the rhodamine spirolactam ring generated by  $\text{Hg}^{2+}$  binding and the 1:1 stoichiometric structure of SRB and  $\text{Hg}^{2+}$  were confirmed. After that,  $\text{CN}^-$  in acetonitrile was detected using an SRB- $\text{Hg}^{2+}$  complex chemosensor in the presence of several anions. Additionally, when  $\text{Hg}^{2+}$  was added, this sensor showed extremely sensitive and selective identification of cyanide ions, changing color to revert to colorless in the identical solution. The application of SRB with the PEGDMA polymer to detect  $\text{Hg}^{2+}$  ions was ultimately successful, and the results were examined using SEM and fluorescent confocal laser scanning microscopy (CLSM) (Fig. 34b) [83].

The High selectivity and sensitivity to  $\text{Hg}^{2+}$  are achieved in the effective design and synthesis of a pair of 1,8-naphthalimide-Rhodamine based chemosensors (65). When it interacts with  $\text{Hg}^{2+}$  in pure  $\text{CH}_3\text{CN}$ , it changes color from yellow to orange and displays a typical fluorescence resonance power transfer signal from 1,8-naphthalimide to Rhodamine 6G. However, RB-NA in  $\text{CH}_3\text{CN}$ /HEPES buffer is limited to its ability to function as a photoinduced electron transfer-off process in 1,8-naphthalimide, with an increase in fluorescence intensity centered at 525 nm upon the addition of  $\text{Hg}^{2+}$ . But in the pure  $\text{CH}_3\text{CN}$  system, the  $\text{Hg}^{2+}$  can open the spirolactam ring of Rhodamine B in RB-NA and block the PET process in 1,8-naphthalimide, which results in the formation of a new emission band at 575 nm and an intensity of fluorescence enhancement at 515 nm, along with a noticeable shift in color from yellow to pink (Fig. 35a) [84]. The rhodamine-based colorimetric and fluorescent sensor (66) for  $\text{Hg}^{2+}$  showed remarkable selectivity and sensitivity, as evidenced by the growing absorption peak at 565 nm and a 32-fold fluorescence amplification at 586 nm with notable color changes. Between 0 and 90  $\mu\text{M}$ , the absorbance and fluorescence maxima increased linearly in proportion to the  $\text{Hg}^{2+}$  concentration. The limits of the colorimetric and fluorescence detection methods were 6.36  $\mu\text{M}$  and 60.78 nM, respectively. It showed good interference immunity and minimal cytotoxicity, and it could operate in a nearly neutral pH range of 6.01–8.57. It was possible to construct a 1:2 sensor- $\text{Hg}^{2+}$  complex with a binding constant of  $2.89 \times 10^8 \text{ M}^{-2}$ . A brand-new sensing method was suggested. It was effectively used for living cell imaging and real sample assay. Moreover, the sensor for signaling  $\text{Hg}^{2+}$  in 100 % aqueous solution may be supported in inexpensive cellulose discs (Fig. 35b) [85].

A new fluorescent chemosensor (67) based on rhodamine 6G for  $\text{Hg}^{2+}$  has been synthesized and validated using NMR and LC-MS methods. In the mixed organic aqueous phase, the fluorescent chemosensor exhibits a strong preference and sensitivity for  $\text{Hg}^{2+}$  over other metal ions. After adding  $\text{Hg}^{2+}$ , there was a noticeable increase in fluorescence and ring-opening of a rhodamine spiro-cyclic structure. The PS- $\text{Hg}^{2+}$  complexes' stoichiometric proportion was found to be 1:1 using the  $^1\text{H}$  NMR experiment and Job's plot. For PS- $\text{Hg}^{2+}$  complexation, the predicted binding constant and limit of detection (LOD) are  $6 \times 10^4 \text{ M}^{-1}$  and  $3.0375 \times 10^{-8} \text{ M}$  (30.37 nM), respectively.  $\text{Hg}^{2+}$  binding in chemosensor PS resulted in an intense fluorescence increase that was most noticeable between pH

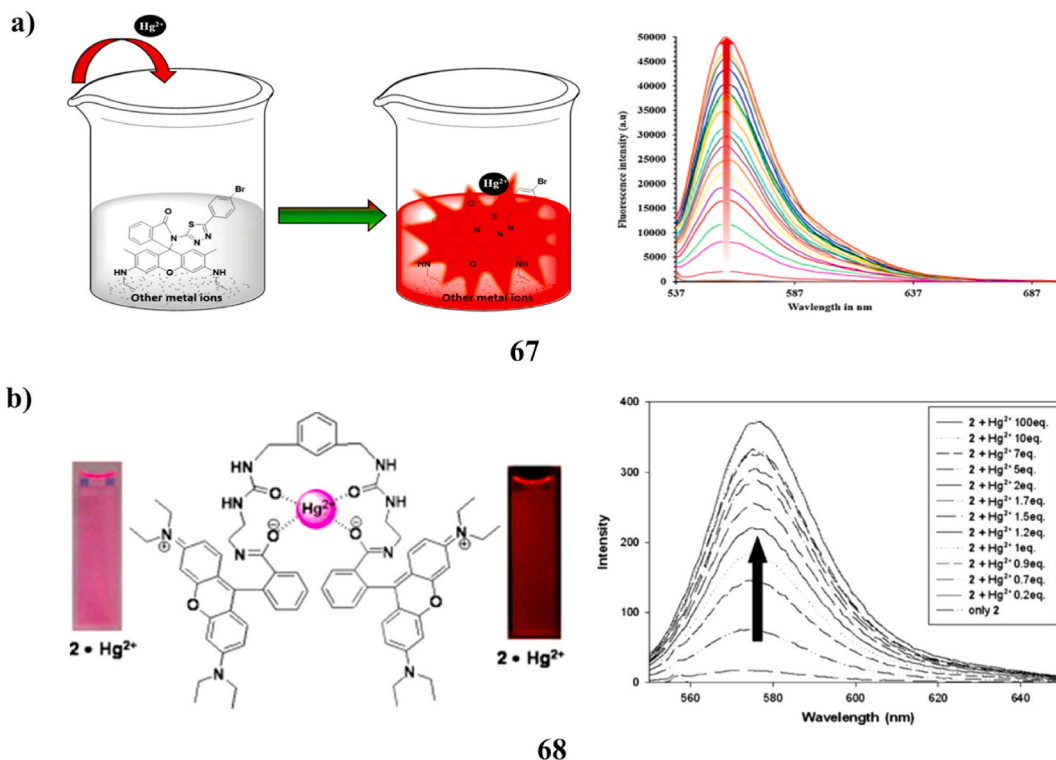
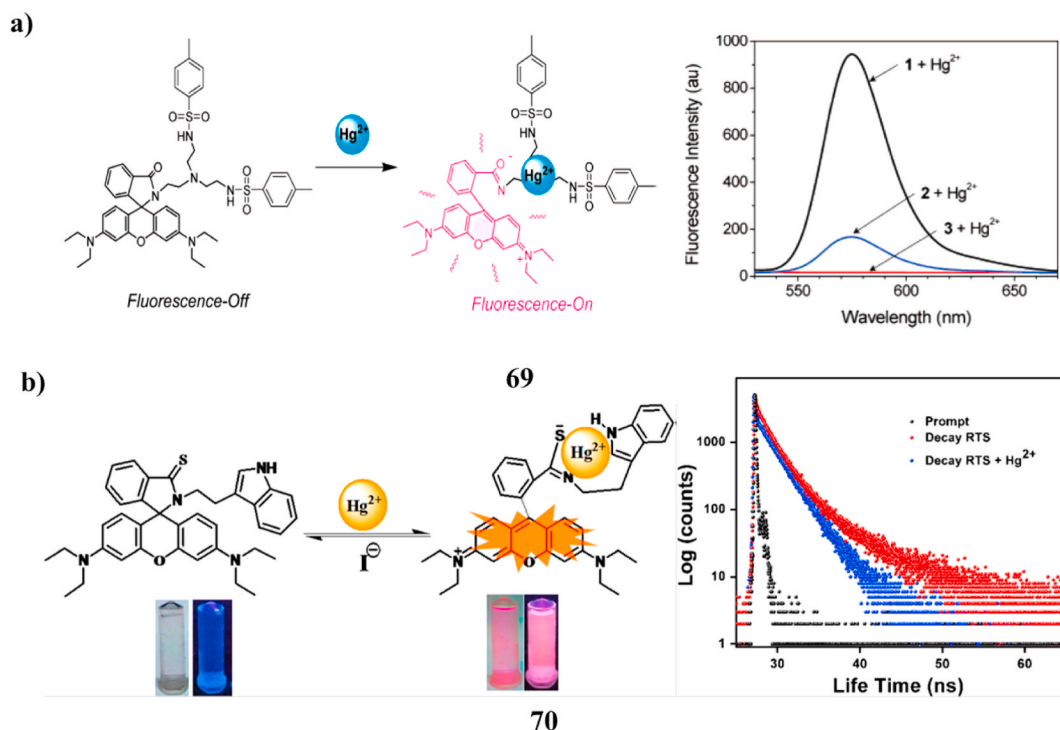


Fig. 36. a). MTT assay method of Rho6G-based  $\text{Hg}^{2+}$  chemosensor (67). b). Photophysical study of RhB-urea based  $\text{Hg}^{2+}$  chemosensors (68).

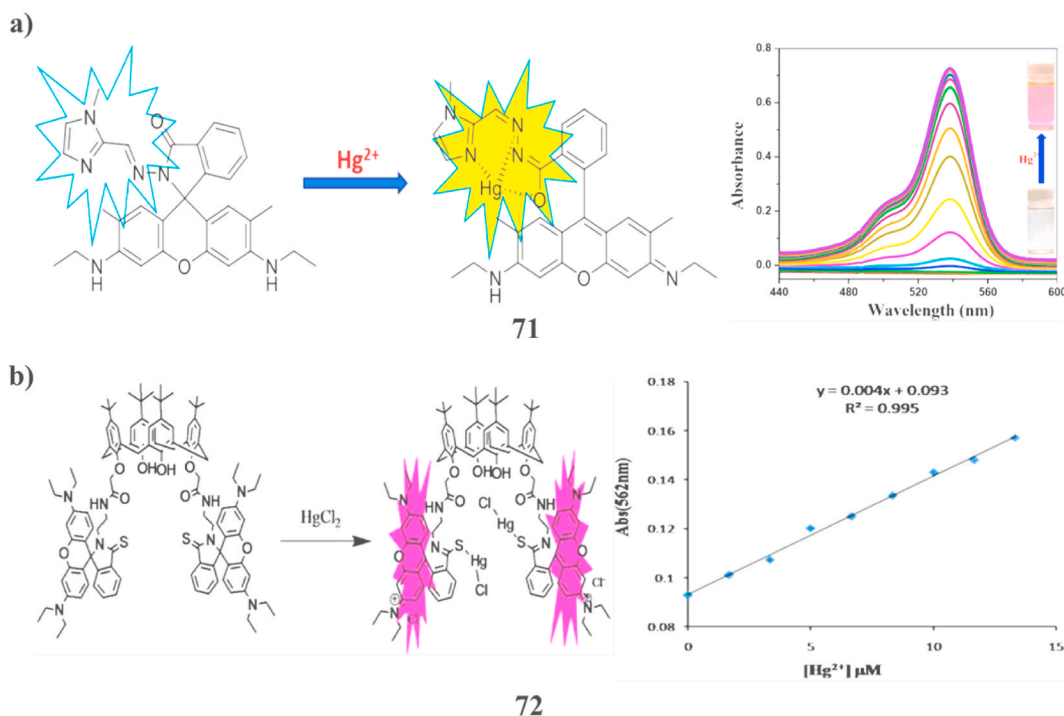
values of 6 and 8. With the use of real water samples and a spike and recovery technique, the  $\text{Hg}^{2+}$  metal ion was efficiently identified. Furthermore, the low-cytotoxic probe PS was employed in a cell scanning experiment employing MDA-MB-231 and A375 breast cancer cells to detect  $\text{Hg}^{2+}$  intracellularly using the MTT assay method (Fig. 36a) [86]. To identify metal ions, novel urea-group containing rhodamine compounds (**68**) have been produced. The dimeric system probe demonstrated a selective fluorescence amplification and colorimetric shift with the addition of  $\text{Hg}^{2+}$ . This probe exploited the ring-opened amide (fluorescent) to spirolactam (nonfluorescent) mechanism. A value of  $3.2 \times 10^5 \text{ M}^{-1}$  was determined for the probe's association constant with  $\text{Hg}^{2+}$  (Fig. 36b) [87].

A tren-based tripodal chemosensor (**69**) with two tosyl groups and rhodamine was created, and UV/vis and fluorescence spectroscopies were used to study the sensor's behavior toward metal ions. The  $\text{Hg}^{2+}$  ion produced a visible color change and significantly increased fluorescence when added to a  $\text{CH}_3\text{CN}$  solution containing the probe producing very minor color/spectral modification. These findings combined to provide a  $\text{Hg}^{2+}$  selective fluorescent chemosensor (OFF-ON) (Fig. 37a) [88]. A new fluorescent and chromogenic chemosensor (**70**, RTS) based on the rhodamine-tryptamine combination for the detection of  $\text{Hg}^{2+}$  in water. A deep pink coloring and a vivid orange fluorescence were seen in an aqueous methanol solution of RTS following the progressive addition of  $\text{Hg}^{2+}$ . The probe showed a significant degree of selectivity towards  $\text{Hg}^{2+}$  as compared to other competing metal ions. Mass spectroscopy and Job's plot analysis were used to determine the 1:1 binding stoichiometry between RTS and  $\text{Hg}^{2+}$ . According to preliminary research, the synthesized probe RTS was very non-toxic and was able to distinguish between intercellular  $\text{Hg}^{2+}$  ions by successfully passing via the cell exteriors of model cell systems, such as human neuroblastoma (SHSY5Y) cells and cervical cells (HeLa). By using fluorescence titration, the limit of detection (LOD) was determined to be 2.1 nM. Furthermore, it has been shown that synthetic chemosensors have potential utility for identifying  $\text{Hg}^{2+}$  ions in ambient fluid samples (Fig. 37b) [89].

A novel fluorescent with colorimetric chemosensor (**71**) utilizing rhodamine 6G as its basis and an N-methyl imidazole nucleus has been developed to enable the selective identification of  $\text{Hg}^{2+}$  ions. The fluorescence spectral examination and UV-Vis data showed that the receptor is sensitive to and selective for  $\text{Hg}^{2+}$ , with no discernible interference from other rival metal ions. It was observed that the addition of  $\text{Hg}^{2+}$  to the receptor caused a rapid color shift from colorless to pink. The sensitivity of several cations to  $\text{Hg}^{2+}$ -inducing fluorescence was examined. Job's graphic provided evidence for the stoichiometric balance of 1:1 involving the receptor and  $\text{Hg}^{2+}$ . The spirolactam ring-opening process was identified as the cause of the color shift and the fluorescence response that occurred with the presence of the  $\text{Hg}^{2+}$  ion.  $^1\text{H}$  NMR and mass spectrum analysis were used to validate the likely manner of interaction between the receptor and  $\text{Hg}^{2+}$ . Its test strips made of electrospun nanofiber were effectively used to identify  $\text{Hg}^{2+}$  ions in an aqueous environment (Fig. 38a) [90]. A thiospirolactam RhB ligand for an efficient colorimetric OFF-ON sensor (**72**) for mercury (II) ions in neutral aqueous conditions is derived from the modified p-tert-butylcalix [4] due to its inherent amphiphilic characteristic. It has been examined using electronic spectroscopy methods. The thiospirocyclic moiety of this ligand allows it to distinguish between different alkali, alkaline earth, and transition metal ions and chronic toxic  $\text{Hg}^{2+}$  ions. The ligand exhibits a  $\text{Hg}^{2+}$  ion detection limit of  $9.65 \times 10^{-9} \text{ M}$  and an association constant of  $3.63 \times 10^5 \text{ M}^{-1}$ . Additionally, this ligand can penetrate HeLa cells, which may be useful in detecting  $\text{Hg}^{2+}$  ions



**Fig. 37.** a). Fluorescence study of Rhodamine-tosyl groups based  $\text{Hg}^{2+}$  Chemosensor (**69**). b). Biological applications of tryptamine-appended rhodamine-based  $\text{Hg}^{2+}$  chemosensor (**70**).



**Fig. 38.** a). Absorption study of RhB based  $Hg^{2+}$  Chemosensor (71). b). Live Cell Imaging study of *p*-tert-Butylcalix [4]arene Thiospirolactam RhB Based Mercury Sensor (72).

in biological systems through the use of fluorescence imaging (Fig. 38b) [91].

Rhodamine-based mercury (II) sensors utilize fluorescence quenching or fluorescence resonance energy transfer (FRET) mechanisms for detection. Upon mercury (II) ion binding, the rhodamine moiety experiences a change in its electronic environment, leading to a measurable decrease in fluorescence intensity or altered emission wavelength. This response facilitates highly sensitive mercury detection. Advantages include high sensitivity, low detection limits, and rapid response times, making these sensors suitable for real-time monitoring in IoT and wearable devices. Limitations involve potential photobleaching and interference from other ions. For instance, rhodamine-based sensors have been employed in wearable devices for environmental monitoring, offering real-time feedback on mercury exposure levels, and demonstrating their practical application in ensuring environmental safety.

A summary of sensors, principles, Detection Mechanism, Advantages, Disadvantages, and Biomaterial applications is found in Table 1 below.

## 8. Conclusion

Recent advancements in photoresponsive-based mercury (II) sensors represent a pivotal step forward in addressing the pressing need for efficient and reliable detection methods. These sensors utilize materials such as azobenzene, coumarin, fluorescein, pyrene, quinoline, and rhodamine, which exhibit changes in optical properties upon interaction with mercury ions, allowing for high sensitivity and selectivity. The integration of cutting-edge materials and emerging technologies like IoT and wearables has endowed these sensors with enhanced capabilities, enabling real-time and remote monitoring. This has broadened their applications beyond traditional environmental monitoring to include bioimaging and personal exposure assessment. For example, coumarin-based sensors offer high quantum yield and rapid response, while fluorescein-based sensors provide strong fluorescence and low detection limits, ideal for cellular imaging. Despite their potential, challenges such as improving multifunctionality, refining selectivity, and enhancing on-site portability remain. Addressing issues like photobleaching, solvent dependency, and potential interference is crucial for further development. Nevertheless, the transformative potential of these sensors in revolutionizing environmental monitoring and public health is undeniable. As research continues, advancements promise to refine our understanding of mercury contamination and catalyze tangible improvements in pollution management and preventative strategies, paving the way for more effective and sustainable solutions.

## Data availability statement

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

**Table 1**

A structured overview of the synthesized sensors, including their performance, detection mechanism, selectivity, limit of detection (LOD), advantages and disadvantages, and biomaterial applications, is provided in this table.

Compounds	Principle	Performance	Detection Mechanism	Selectivity	Limit of Detection (LOD)	Advantages	Disadvantages	Biomaterial Applications
Azobenzene	Photoisomerization changes upon binding with Hg(II)	High sensitivity, quick response	Optical signal change	Moderate, influenced by pH	$\mu\text{M}$ to nM range	Reversible, easy synthesis	Limited selectivity, possible interference	Imaging and sensing in biological systems, drug delivery
Coumarin	Fluorescence quenching or enhancement upon binding with Hg(II)	High sensitivity, rapid response	Fluorescence emission change	Good, often tailored for Hg (II)	nM to pM range	High quantum yield, tunable properties	Photobleaching, solvent-dependent fluorescence	Bioimaging, fluorescent probes in living cells
Fluorescein	Fluorescence intensity changes upon interaction with Hg(II)	Excellent sensitivity, quick detection	Fluorescence intensity change	High, can be modified for selectivity	pM range	Strong fluorescence, high molar absorptivity	Photobleaching, pH sensitivity	Cellular imaging, pH sensors, molecular probes
Pyrene	Fluorescence quenching or enhancement upon binding with Hg(II)	High sensitivity, good performance	Fluorescence emission change	Good, selective for Hg(II)	nM to pM range	High fluorescence, long lifetime	Limited water solubility, potential toxicity	Biosensors, environmental monitoring, cell imaging
Quinoline	Fluorescence change or chelation induced by Hg(II)	High sensitivity, rapid response	Fluorescence signal change	Good, can be modified for selectivity	nM range	Versatile, easy functionalization	Photostability issues, solvent effects	Bioimaging, fluorescent probes, metal ion detection in cells
Rhodamine	Fluorescence "off-on" change due to Hg(II) induced spirocyclic ring opening	Excellent sensitivity, fast response	Fluorescence "off-on" signal change	High, specific for Hg(II)	pM to nM range	High fluorescence quantum yield, water-soluble	Photobleaching, possible interference	Cellular imaging, tracking of metal ions in biological systems

## CRediT authorship contribution statement

**Mani Rajasekar:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision. **Chiterasu Narendran:** Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Jennita Mary:** Methodology, Investigation, Funding acquisition, Formal analysis. **Sivakumar Meenambigai:** Software, Resources, Project administration, Methodology.

## 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.

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