RJC

RASĀYAN *J. Chem.*
Vol. 18 | No. 1 |373-379| January - March | 2025
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

SYNTHESIS OF QUINOLINE-BASED THERMO RESPONSIVE POLYMERIC GEL AND APPLICATION IN EFFICIENT FLUOROPHORIC DETECTION OF Hg^{2+} IONS

S. Sehlangia[1], R. Mukherjee[2], L. Kaur[3], Raffiunnisa[4], Vaishali. N. Agme[5], A. Tewari[6] and A. K. Tripathi[7,✉]

[1]Department of Chemical Science, Indian Institute of Technology, Mandi-175005, (Himachal Pradesh) India
[2]Department of Chemistry, Dum Dum Motijheel College, Kolkata-700074, (West Bengal) India
[3]Department of Nutrition and Dietetics, Manav Rachna International Institute of Research and Studies, Faridabad-121004, (Haryana) India
[4]Department of Chemistry, Aditya University, Surampalem-533437, (Andhra Pradesh) India
[5]Department of Applied Science, Bharati Vidyapeeth College of Engineering, Navi Mumbai-410210, (Maharashtra) India
[6]Basic Science and Humanities, Pranveer Singh Institute of Technology, Bhauti, Kanpur-209305, (Utter Pradesh) India
[7]Department of Chemistry, DDU Gorakhpur University, Gorakhpur-273001, (Uttar Pradesh) India
✉Corresponding author: abhiktripathi@outlook.com

ABSTRACT

This paper reports an effective approach for fabricating a thermo-responsive gel polymer based on dithioacetylation of quinoline-2,4-dicarbaldehyde and used as a sensor for detecting metal ions. The synthesis was confirmed using NMR spectroscopy. The effect of varying temperatures and solvents was investigated for the formation of the polymeric gel, and the formation mechanism was explained. The synthesized polymer was used to detect the Hg^{2+} ions in various samples. The polymer showed turn-on-fluorescence sensitivity to Hg^{2+} ion with excellent photoluminescence properties, and fluorescence emission was achieved at 418 nm. The polymer's ability to sense Hg^{2+} ions was tested by analyzing different samples from different sources at a nanomolar scale. The effect of increasing the concentration of the Hg^{2+} ions on polymeric gel's durability and fluorescence sensing was investigated. The method was validated, and the limit of detection and quantification were calculated. The DFT calculations were performed to develop the lowest energy structures and HOMO-LUMO orbitals of the QNS-polymer.

Keywords: Quinoline, Dithioacetylation, Polymeric Gel, Fluorophoric Chemosensing, Metal Ions.

RASĀYAN *J. Chem.*, Vol. 18, No.1, 2025

INTRODUCTION

The detection of harmful metal ions from environmental and biological samples is very important and challenging.[1] Until now, multiple kinds of literature on sensing metal ions in aqueous samples have been reported where small molecule or macromolecule-based chemosensors have been used to detect the different metal ions.[2-6] Among them, the fluorescence detection methods are considered supreme due to the specific range of fluorescence emission of the chemosensor with particular metal ions.[2,4] Till now, polymer-based sensors have not been well explored for sensing purposes. The polymer base sensors will advance more than single molecular chemosensors due to repeating desired units. Polymers are wildly used substances/materials in many applications today, including petrochemicals, cosmetic, biomedical, solar cells, lithium-ion batteries, water filtration, drug delivery, polymeric gel, nanoparticles, space technology, food, household materials, self-healing materials, electronic and magnetic materials, and luminescent materials, etc.[7-14] The use of the polymer for different applications depends on the types of monomer units used in synthesis. Quinolines are aromatic compounds that naturally arise as fused rings that belong to a heterocyclic class. Numerous industrial and medical uses have been found for quinoline and its

http://doi.org/10.31788/RJC.2025.1819128

derivatives.[2-4] Due to its unique coordination and photophysical properties, the substituted quinoline received excellent attention among the chromophores employed to create luminous materials.[15,16] The quinolines exhibit exceptional luminescence and fluorescence because of the fused ring aromatic structure. Thus, there has been a lot of interest in developing fluorescent and luminous materials. The heteroatom (nitrogen atom) in quinoline acts as an electro-donor group. It shows high binding capacity with various analytes when used as a chemosensor, such as styryl-substituted 8-hydroxyquinoline derivatives.[2,4] Chemosensors based on quinoline derivatives have been used to detect a range of metal cations.[2-4,18] The present report describes the synthesis of a new quinoline-based polymer via condensation polymerization. The carboxylic groups of the quinoline-2,4-dicarboxylic acid were first converted to aldehyde groups, and then quinoline-2,4-dicarbaldehyde was modified with 2,2′-(Ethylenedioxy)diethanethiol in a dithioacetalization reaction, and a cross-linked 3D polymer was obtained (Scheme-1). In the presence of suitable solvents, the synthesized polymer forms thermo-responsive gel, which loses its gel form when heated at high temperatures. The formation of the polymeric gel with varying solvents and temperature conditions were studied. The durability of the polymeric gel was examined with various metal ions. A selective turn-on fluorescence detection method for the Hg^{2+} ions using the prepared polymer was studied and validated. The effect of the other metal ions on the detection sensitivity of the Hg^{2+} ions was investigated. Additionally, the stable structure, HOMO-LUMO, and energy gap optimizations were carried out by DFT simulations. The system's sensitiveness and selectivity towards the Hg^{2+} ions were determined.

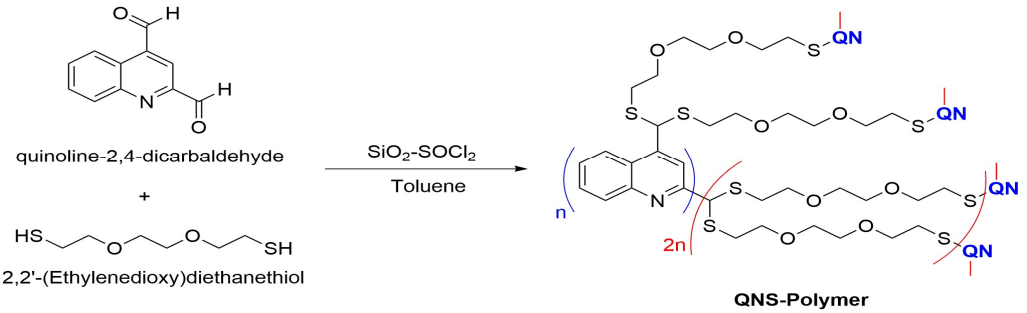
EXPERIMENTAL

Material and Methods

Quinoline-2,4-dicarboxylic acid, 2,2′-(Ethylenedioxy)diethanethiol, *fac*-Ir(ppy)$_3$, tris(trimethylsilyl)silane, K_2HPO_4 and NMR solvents were ordered from Sigma-Aldrich. The environmental water samples were collected from nearby locations. Avra Chemicals (India) supplied this investigation's solvent and other reagents.

Instruments and Equipment

FT-IR spectrophotometer (Agilent), UV-2450 spectrophotometer (Shimadzu), Fluorescence spectrometer (Agilent), HR-MS (Bruker HD), NMR instrument (Jeol 500 MHz) and CHNS-elemental analyzer were used to characterized synthesis products.



Scheme-1: Synthesis of QNS-Polymer from Quinoline-2,4-dicarbaldehyde and 2,2′-(Ethylenedioxy)diethanethiol.

Synthesis of Quinoline-2,4-dicarbadlehyde

The quinoline-2,4-dicarbaldehyde from quinoline-2,4-dicarboxylic acid was prepared using *fac*-Ir(ppy)$_3$ catalyst as described in the literature.[19] A pale yellowish-brown solid (yield 89%) was obtained from chromatography. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.04 (s, 1H), 9.95 (s, 1H), 8.51 – 8.45 (m, 1H), 8.38 (s, 1H), 8.26 (dd, J = 7.5, 1.6 Hz, 1H), 7.87 (td, J = 7.2, 1.3 Hz, 1H), 7.66 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H).

SiO_2-$SOCl_2$ Catalyst

Under stirring, 20 g silica gel was added to 40 mL Dry DCM, and then 20 g $SOCl_2$ was added dropwise to this mixture. The resulting solution was stirred for 1 hour. SO_2 and HCl released during this reaction confirm the formation of SiO_2-$SOCl_2$. After the reaction, the solvent and reaming $SOCl_2$ were removed under a vacuum, and the dried product was directly used as a catalyst for the polymerization reaction.[20]

Polymerization (Dithioacetalization)

Quinoline-2,4-dicarbaldehyde (1 mmol) and SiO_2-$SOCl_2$ (0.4 g) were added to a 15 mL solution of dithiol (2,2′-(Ethylenedioxy)diethanethiol; 2.1 mmol) in dry toluene. The reaction mixture was stirred for 9 hours at 65 °C.[20] The progress of the reaction was monitored with TLC. Silica gel and product were filtered off, loaded in a small column, and washed thoroughly with DCM to remove unreacted substrates and isolate the desired product. The DCM was then removed under reduced pressure, and the desired product was obtained (yield 84%). The polymer synthesis was confirmed using NMR spectroscopy (Fig.-1). The average molecular weight of the synthesized polymer was obtained using gel permeation chromatography (styrene-based standard was used), and the obtained average molecular weight was 19198 g/mol.

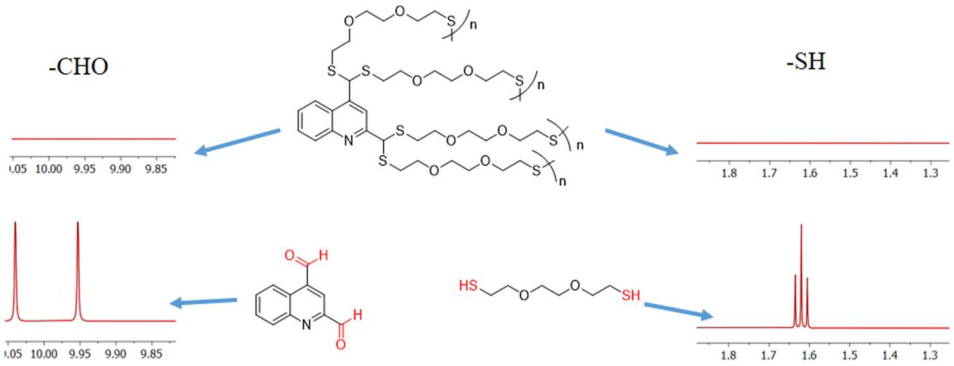


Fig.-1: The Confirmation of the Synthesis of QNS- Polymer

Preparation of Gel

In a glass vial, the quinoline-dithiol (QNS)-polymer and dioxane were mixed in a 1:80 molar ratio, and a non-sticky pale yellowish gel was formed. Similarly, other solvents (benzene, diethyl ether, and THF) and a mixture of solvents (dioxane and THF) were used to prepare the polymer gel. The gel prepared in dioxane is shown in Fig.-2.

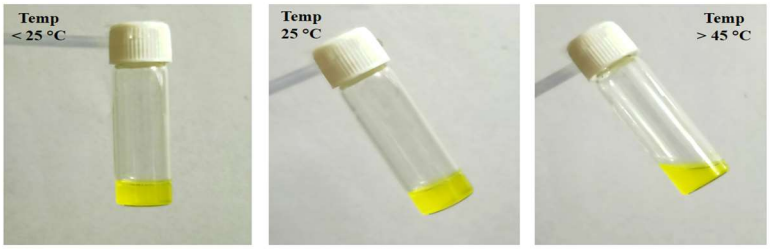


Fig.-2: Effect of the Temperature on the Prepared QNS-Polymer-Based Gel in Dioxane

Reaction of QNS-Polymer with Mercury Ions

The stranded solution of 20 mM Phosphate-buffered saline (PBS) was prepared as reported in the literature.[21] The solution of 0.5 µM QNS-Polymer in ACN was mixed with aqueous Hg^{2+} solution (1 to 5 equivalent) and 20 mM PBS buffer (7.5 pH). The prepared solutions were incubated for 45 min before fluorescence detection studies. The different organic solvents, pH of the buffer, and concentration ratio of solutions of QNS-polymer and Hg^{2+} ions for fluorescence detection study were investigated.

RESULTS AND DISCUSSION

Synthesis of Aldehyde from Acids

The carboxylic groups of the quinoline-2,4-dicarboxylic acid were directly converted to aldehydes in the presence of a photo redox catalyst [*fac*-Ir(ppy)$_3$] followed by a reductive-oxidation reaction.[19] K_2HPO_4 and tris(trimethylsilyl)silane were used as base and hydrogen sources, respectively, in the reaction. The single electron transfer (SET) mechanism occurred during the synthesis, yielding 89% quinoline-2,4-dicarbadlehyde. The polar aprotic solvent acetonitrile (ACN) was found suitable for the reaction. The

nitrogen of quinoline and solvent didn't interfere with the SET mechanism during the reaction. The synthesis of the compound was confirmed by NMR and HRMS.

Polymerization via Dithioacetalization

The polymerization was carried out via a dithioacetalization reaction of quinoline-2,4-dicarbaldehyde and 2,2′-(Ethylenedioxy)diethanethiol in the presence of SiO_2-$SOCl_2$ catalyst (Scheme-1).[20] The SiO_2-$SOCl_2$ catalyst was prepared by the addition of $SOCl_2$ into silica gel solution under dry conditions. The $SOCl_2$ vigorously reacts with silica gel and activates its surface by replacing one oxygen atom with the chlorine atom. The release of SO_2 gas is direct evidence of the formation of a SiO_2-$SOCl_2$ catalyst.[20] SiO_2-$SOCl_2$ catalyst allows to adsorbed the aldehydes group of quinoline-2,4-dicarbaldehyde on its surface, followed by the substitution reaction of two thiol molecules [2,2′-(Ethylenedioxy)diethanethiol] substitute the aldehydic oxygen atom and form cross-link QNS-polymer. The synthesis conditions were investigated by modifying the solvents, catalyst, adding base, reaction time, etc. The use of silica gel in the reaction (without modifying to SiO_2-$SOCl_2$) produces poor yield. The dry toluene as a solvent in reaction yielded 84% conversion of the quinoline-2,4-dicarbaldehyde and 2,2′-(Ethylenedioxy)diethanethiol to cross-linked QNS-polymer but dry solvents such as acetone, benzene, diethyl ether, acetonitrile, dichloromethane and THF cause low yield (20-65%) of polymerization. The suitable temperature condition for the reaction was investigated by varying the temperature to 10-110 °C. Heating the reaction mixture at 65 °C temperature in dry toluene was optimal for the reaction and yielded the highest. The disappearance of the peaks of the hydrogen of the aldehyde and thiol groups confirmed the synthesis of the polymer.

Gel Properties of the Polymer and Thermal Stability

The prepared cross-linked polymer turns into a gel in the presence of polar aprotic solvents and non-polar solvents. The dioxane forms a durable gel compared to other solvents such as diethyl ether, THF, benzene, etc.[22] The high polarity of the solvent makes the polymer soluble in solvents. The gel formation was carried out using dioxane, and its durability with temperature was examined. When the polymer is exposed to dioxane, it starts to swallow, and increasing its concentration leads to the formation of a non-sticky gel. The concentration of the polymer and dioxane was varied to 1:30, 1:50, 1:80, 1:100, 1:120, and 1:150 molar ratios. The solvent and polymer ratio 80:1 was found suitable for preparing polymeric gel. Similarly, the polymeric gels were prepared using benzene, diethyl ether, and THF solvents. The higher concentration of the solvent leads to dissolve the gel and form a polymer solution. Polar solvents were unable to form a polymeric gel. The mix solvents such as dioxane and THF or acetonitrile (1:1) were also tested in preparation of the polymer base gel for fluorescence studies. The polymer-based gel formed in dioxane was more durable than the gels formed with other solvents but was sensitive to high temperatures.[22,23] Thus, the effect of heating the gel at different temperatures was investigated. Synthesized gel shows high stability at room temperature or moderated temperature. However, increasing the temperature above 45-55 °C leads to the deformation of the gel into a liquid solution. The effect of heating on the gel is shown in Fig.-2.

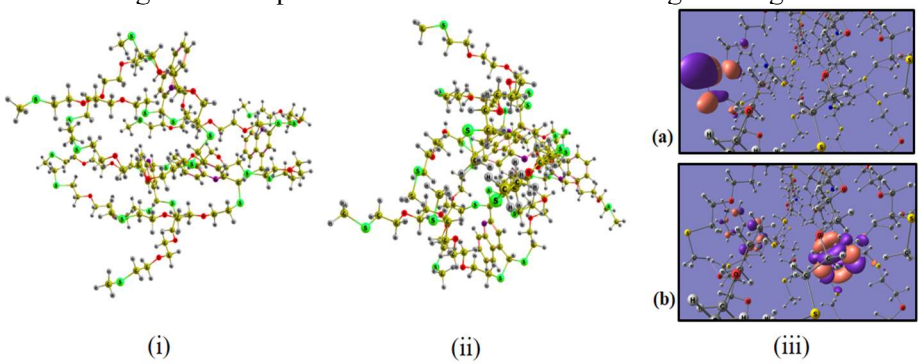


Fig.-3: The 3D Cross-Linked Structure (Globular Structure) of the Fragment of the Prepared QNS-Polymer [(i). Front View and (ii) Side View] and (iii) Homo-Lumo Orbitals

Shape of the Polymer (3D polymer Figure) and Mechanism of the Metal Ions Detection

The 3D structure and homo-lumo orbitals of a polymer fragment were developed using the Gaussian program.[24,25] The 3D structure shows the formation of a random cross-linked polymer (Fig.-3), which forms

a globular structure, most likely the proteins do. The globular structure allows the entry of desired ions or small molecules into the cavity or gaps between the polymers and shows strong binding inside due to less interference. Due to a high number of polar atoms, the metal cations easily interact with the QNS-polymer via ionic interactions. In the case of Hg^{2+} ion, it has an excellent affinity with sulfur atoms and thus interacts strongly with the dithioacetal group and breaks it down.[21] The de-acetalization of QNS-polymer with Hg^{2+} ions forms quinoline-2,4-dicarbaldehyde, which is a highly luminescent compound. Therefore, this polymer is used for fluorophoric detection of the Hg^{2+} ion.

Fluorescence Sensing of Hg^{++}

In this report, a turn-on fluorescence method was described. The prepared polymer was used in selective sensing of the Hg^{2+} ions because the dithioacetal group has an excellent affinity to bind with Hg^{2+} ions. As a result, the dithioacetal group break and aldehydes groups are obtained.[21] The dithioacetal group on the quinoline molecule quenches the fluorescence properties of the polymer; thus, the polymer shows very low emission in the fluorescence region.[21] When the prepared polymer was mixed with a solution of Hg^{2+} ion, the mercury bound strongly with the dithioacetal group; thus, the polymer started to degrade to quinoline-2,4-dicarbaldehyde, and it showed high fluorescence emission in the fluorescence region. Therefore, the polymer acts as a turn-on fluorescence chemosensor for Hg^{2+} ions. Due to the presence of appropriate binding sites in the QNS-polymer, we wished to investigate the chemosensing ability of Hg^{2+} metal ion in the presence and absence of the other metal ions such as Ag^{+}, Al^{3+}, Na^{+}, Cr^{3+}, Ni^{2+}, Pb^{2+}, Fe^{3+}, Cd^{2+}, Co^{2+}, Zn^{2+}, and Cu^{2+}. The Mercury ions are known to be dangerous environmental pollutants that can be hazardous to health when present in even low quantities.[25] The individual solution of Ag^{+}, Al^{3+}, Na^{+}, Cr^{3+}, Ni^{2+}, Pb^{2+}, Fe^{3+}, Cd^{2+}, Co^{2+}, Zn^{2+}, and Cu^{2+} ions when mixed with the solution of the polymer, no significant change in the fluorescence spectrum was observed, except Hg^{2+}. The polymer solution showed intense peak fluorescence spectra at 418 nm when treated with Hg^{2+} ions solution (Figures 4(i) display the typical fluorescence spectra of QNS-polymer). The polymer solution in ACN with PBS buffer containing 0.25% DMSO produced excellent results for fluorophoric detection of the Hg^{2+} ions. Increasing the equivalent ratio (0 to 50 equivalent) of the Hg^{2+} ions solution concerning the 0.5 μM QNS-polymer solution gave a more intense fluorescence spectrum. Increasing the heating time of the Hg^{2+} ions and QNS-polymer solution reduces the need for high equivalents of the Hg^{2+} ions. The 30 equivalent concentrations of the Hg^{2+} ions solution produced the highest fluorescence emission with 0.5 μM QNS-polymer solution Fig.-4(i). The dethioacetalation reaction proceeds faster in the presence of the PBS buffer and DMSO.[21] The detection limit (LOD) of the prepared chemosensors (polymer) for Hg^{2+} ions was estimated.[26,27] The IUPAC guidelines define a standard relationship (i.e. LOD = (3.3 x standard deviation)/slope) to determine the LOD values. Also, ten blank samples were taken and measured to determine the relative standard deviation in the current studies. The calculated LOD value of QNS-polymer was 14.53 nM, towards Hg^{2+}, Fig.-4(ii). The binding constant of the chemosensor towards Hg^{2+} was found to be 7.58×10^{4} M^{-1}, using the Benesi-Hildebrand method. To evaluate the excellent selectivity of QNS-polymer towards Hg^{2+} ions, we conducted comparative experiments with various cations (Ag^{+}, Al^{3+}, Na^{+}, Cr^{3+}, Ni^{2+}, Pb^{2+}, Fe^{3+}, Cd^{2+}, Hg^{2+}, Zn^{2+}, and Cu^{2+}) present under similar experimental circumstances. These studies demonstrated that the capacity of QNS to detect Hg^{2+} was not considerably hindered by other metal cations Fig.-4(iii). As a result, QNS is an incredibly selective fluorescence chemosensor for Hg^{2+} identification.

Analysis of River Water

To do this analysis, we prepared two sample solutions of river water, A and B. Sample A contained only a riverwater sample that was boiled for five to ten minutes. Sample B was prepared purposefully by adding a known amount of Hg^{2+} ions in river water. Similar analyzing conditions were applied for both river water samples to detect Hg^{2+} ions, as described earlier in this report. Both samples were tested separately with QNS-polymer solution (0.5 μM), and similar results were obtained, as provided in Fig.-4. The addition of sample A to this solution (QNS-polymer in ACN + PBS+ DMSO) did not appreciably change the fluorescence intensity. However, once sample B containing Hg^{2+} ions was added, the intensity of the QNS-polymer solution fluorescence was enhanced (turn-on). In river water, the detection limit for QNS-polymer (as chemosensor) towards Hg^{2+} was calculated to be 14.72 nM, which was found to be the same as calculated for standard Hg^{2+} ions solution.

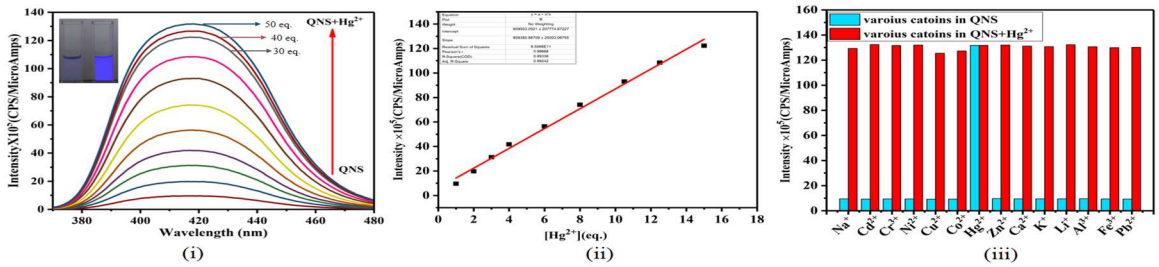


Fig.-4: (i) Fluorescence Spectra of QNS-Polymer (0.5 µM) upon Incremental Addition of Hg^{2+} Concentration (0 to 50 Equivalent), (ii) The Limit of Detection of QNS with $Hg^{2+}$and (iii) Fluorescence Response of QNS upon Addition of Different Metal Ions (Blue Bars), Followed by Addition of Hg^{2+} (red bars).

CONCLUSION

This report has proposed and synthesized quinoline-based dithioacetal groups containing a cross-linked polymer. The gel formation ability and Thermo-responsive behavior of the polymer were studied in different solvents and temperature conditions. The QNS polymer showed great affinity and fluorescence sensitivity for Hg^{2+} ions and detected them very efficiently in the nanomolar concentration range. Chemical analysis may be utilized with these polymeric chemosensors to detect Hg^{2+} ion traces in rivers and other waste and can be used in the bioimaging of living cells. In conclusion, tuneable chemosensors based on polymeric quinoline-dithioacetal moieties have been generated for the first time, forming a unique class of well-defined chemosensors. In addition to the chemosensor applications under investigation in this work, previous research indicates that these compounds have significant promise as electroluminescent and electron-transport materials. Analyzing similar chemosensors' characteristics can lead to their development with considerable promise for the aforementioned uses.

ACKNOWLEDGMENTS

The authors are grateful to Indian Institute of Technology Mandi, DDU Gorakhpur University and Dum Dum Motijheel College (Kolkata) for providing necessary facilities.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

S. Sehlangia https://orcid.org/0000-0001-7857-9583
R. Mukherjee https://orcid.org/0009-0005-9964-5822
L. Kaur https://orcid.org/0000-0002-4634-7355
Raffiunnisa https://orcid.org/0009-0008-4281-6653
V. N. Agme https://orcid.org/0000-0002-2652-7404
A. Tewari https://orcid.org/0000-0002-1456-649X
A. K. Tripathi https://orcid.org/0000-0003-1210-9516

REFERENCES

1. M. B. Gumpu, S. Sethuraman, U. M. Krishnan and J. B. B. Rayappan, *Sensors and Actuators B: Chemical* **213** , 515(2015), https://doi.org/10.1016/j.snb.2015.02.122
2. S. Sehlangia, N. Nayak, N. Garg, and C. P. Pradeep, *ACS Omega*, 7(28), 24838(2022), https://doi.org/10.1021/acsomega.2c03047
3. S. Sehlangia, M. Devi, N. Nayak, N. Garg, A. Dhir and C. P. Pradeep, *ChemistrySelect*, **5**, 5429 (2020), https://doi.org/10.1002/slct.202000674

4. S. Sehlangia, S. Sharma, S. K. Sharma and C. P. Pradeep, *Materials Advances,* **2**, 4643(2021), https://doi.org/10.1039/D1MA00215E
5. Y. Xiao, X. Yang, X. Cheng, S. Xiong and R. Chen, *Materials Research Express*, **7**, 105304(2020), https://doi.org/10.1088/2053-1591/abbbab
6. D. Wang, L. Marin and X. Cheng, *International Journal of Biological Macromolecules*, **198**, 194(2022), https://doi.org/10.1016/j.ijbiomac.2021.12.075
7. Y. Pan, J. Bai, G. Yang and Z. Li, *Molecules,* **28(23)**, 7934(2023), https://doi.org/10.3390/molecules28237934
8. T. F. R. Alves, M. Morsink, F. Batain, M. V. Chaud, T. Almeida, D. A. Fernandes, C. F. da Silva, E. B. Souto and P. Severino, *Cosmetics*, **7(4)**, 75(2020), https://doi.org/10.3390/cosmetics7040075
9. Q. Liao, E. J. Kim, Y. Tang, H. Xu, D. G. Yu, W. Song and B. J. Kim, *Porous Organic Polymers*, **62**, 1517(2024), https://doi.org/10.1002/pol.20230270
10. Q. He, J. Ning, H. Chen, Z. Jiang, J. Wang, D. Chen, C. Zhao, Z. Liu, I. F. Perepichka, H. Meng and W. Huang, *Chemical Society Reviews*, **53**, 7091(2024), https://doi.org/10.1039/D4CS00366G
11. W. Yu, L. Xiong, J. Teng, C. Chen, B. Li, L. Zhao, H. Lin and L. Shen, *Desalination*, **574**, 117280(2024), https://doi.org/10.1016/j.desal.2023.117280
12. S. Zhang, R. Li and Z. An, *Angewandte Chemie*, **136**, e202315849(2024), https://doi.org/10.1002/ange.202315849
13. I. Roppolo, M. Caprioli, C. F. Pirri and S. Magdassi, *Advanced Materials*, **36**, 2305537(2024), https://doi.org/10.1002/adma.202305537
14. H. A. Alsalmah, A. Rajeh and O. Nur, *Ceramics International*, **50**, 12167(2024), https://doi.org/10.1016/j.ceramint.2024.01.120
15. M. Albrecht, M. Fiege and O. Osetska, *Coordination Chemistry Reviews,* **252**, 812(2008), https://doi.org/10.1016/j.ccr.2007.06.003
16. S. Alwera, and R. Bhushan, *Biomedical Chromatography*, **30**, 1772(2016), https://doi.org/10.1002/bmc.3752
17. P. Patil, P. S. Sehlangia, A. Patil, C. Pradeep, S. K. Sahoo and U. Patil, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,* **220**, 117129(2019), https://doi.org/10.1016/j.saa.2019.05.03
18. S. Alwera, *ACS Sustainable Chemistry and Engineering,* **6,** 11653(2018), https://doi.org/10.1021/acssuschemeng.8b01869
19. M. Zhang, N. Li, X. Tao, R. Ruzi, S. Yu and C. Zhu, *Chemical Communications*, **53**, 10228(2017), https://doi.org/10.1039/C7CC05570F
20. Y. Kamitori, M. Hojo, R. Masuda, T. Kimura and T. Yoshida, *The Journal of Organic Chemistry*, **51**, 1427(1986), https://doi.org/10.1021/jo00359a009
21. C. Song, W. Yang, N. Zhou, R. Qian, Y. Zhang, K. Lou, R. Wanga and W. Wang, *Chemical Communications*, **51**, 4443(2015), https://doi.org/10.1039/C5CC00295H
22. Q. Zhao, J. Sun, Q. Ling and Q. Zhou, *Journal of Polymer Science*, **46**, 6594(2008), https://doi.org/10.1002/pola.22969
23. Y. Nishiyama and M. Satoh, *Journal of Polymer Science*, **38**, 2791(2000), https://doi.org/10.1002/1099-0488(20001101)38:21%3C2791::AID-POLB80%3E3.0.CO;2-1
24. S. Alwera and R. Bhushan, *Biomedical Chromatography*, **30(8)**, 1223(2016), https://doi.org/10.1002/bmc.3671
25. Y. S. Wu, A. I. Osman, M. Hosny, A. M. Elgarahy, A. S. Eltaweil, D. W. Rooney, Z. Chen, N. S. Rahim, M. Sekar, S. C. B. Gopinath, N. N. I. M. Rani, K. Batumalaie and P. S. Yap, *ACS Omega,* **9**, 5100(2024), https://doi.org/10.1021/acsomega.3c07047
26. P. P. M. Deshmukh, P. T. Giri, A. B. Ghogare, N. V. Waghmare, S. Kale, S. K. Singh, B. Kumar, D. S. Baghel, S. Singh, K. Sudhakar and N. K. Pandey, *Rasayan Journal of Chemistry*, **17(2)**, 343(2024), http://doi.org/10.31788/RJC.2024.1728757
27. M. Gopi, T. S. Prasad, D. Ramadevi and K. Basavaiah, *Rasayan Journal of Chemistry*, **17(2)**, 552(2024), http://doi.org/10.31788/RJC.2024.1728793

[RJC-9128/2024]