

Caprolactone-Based Biodegradable Polymer for Selective, Sensitive Detection and Removal of Cu²⁺ Ions from Water

Published as part of the ACS Polymers Au virtual special issue "Polymer Science and Engineering in India".

Narayan Das, Tapendu Samanta, Srishti Gautam, Karina Khan, Susmita Roy, and Raja Shunmugam*



Cite This: *ACS Polym. Au* 2024, 4, 247–254



Read Online

ACCESS |

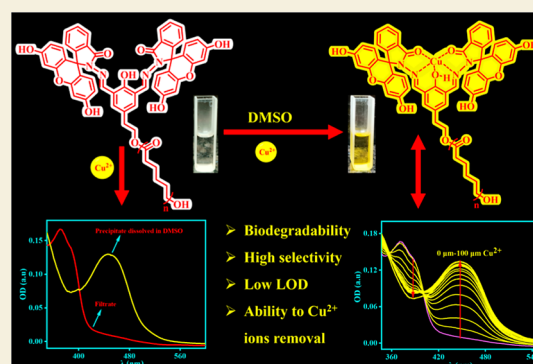
Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: Even though heavy and transition metals originated in the earth's crust, the significant human exposure and environmental pollution consequences of anthropogenic activities include industrial production and waste, mining and smelting operations, and agricultural and domestic usage of metals. Because of their nonbiodegradable nature, heavy metal ions such as Cu²⁺ accumulate very quickly in plants and edible animals, ultimately ending up in the human food cycle. Therefore, to nullify the detrimental effects of Cu²⁺ ions for the sake of the environment and living organisms, we are motivated to design a sensor molecule that can not only detect Cu²⁺ ions but also remove them selectively from the water medium. To detect the Cu²⁺ ions, we synthesized a monomer (NCu) and its biodegradable caprolactone-based polymer (PNCu). It was observed that both NCu and PNCu showed higher selectivity toward Cu²⁺ ions by changing the color from colorless to yellow, with a limit of detection value of 29 nM and 0.3 μM. Furthermore, removing the Cu²⁺ ions from the water solution was also accomplished by introducing the hydrophobicity of the polymer (PNCu) through the ring-opening polymerization process. Due to increased hydrophobicity, the polymer produced a yellow color precipitate upon adding Cu²⁺ ions to the solution; thus, removal of the metal ion is possible using our designed polymer and its detection ability. We checked the removal efficiency of our polymer by using UV–vis spectroscopy and EDX analysis, which indicated that almost all of the copper is removed by our polymer. Therefore, to our knowledge, this is the first biodegradable caprolactone-based polymer for colorimetric turn-on detection and separation of the Cu²⁺ ions from the water.

KEYWORDS: *copper, colorimetric sensor, UV–vis spectroscopy, biodegradable polymer, copper removal*



INTRODUCTION

Even though heavy and transition metals originated during the earth's crust formation, the majority of human exposure and environmental pollution originated from anthropogenic activities, including industrial output and waste production, mining and smelting operations, and agricultural and domestic usage of metals.^{1–4} Environmental heavy metal pollution can also take place through metal evaporation and sediment resuspension from water sources to groundwater and soil, soil erosion of heavy metal ions and leakage of heavy metals, heavy metal corrosion, and atmospheric deposition.⁵ Industrial sources such as petroleum combustion, coal burning in power plants, metal processing in refineries, wood preservation, nuclear power stations, high-tension lines, textiles, microelectronics, plastics, and paper processing plants cause serious heavy metal pollution.^{6–8} Because of their nonbiodegradability, heavy metal ions such as Cu²⁺ accumulate very easily in plants and edible animals, ultimately ending up in the human food cycle.⁹ Copper has a high electrical and thermal conductivity, which is the reason for its higher usage in industrial purposes

after iron and aluminum. Despite essential trace elements, copper originates the complications associated with neurodegenerative diseases, for example, Menkes, Alzheimer's, Parkinson's, and Wilson's diseases.¹⁰ As stated by USEPA (the United States Environmental Protection Agency), the acceptable amount of copper ions in drinking water is 20 mM.¹¹ Because of its vast usage in biotechnology, chemistry, life science, and medicine, copper has appeared as a substantial metal contaminant in the environment.¹² Although copper ions exhibit very low metal toxicity compared with the other heavy toxic metals in leaving organisms, very few specific organisms get contaminated even at minimal submicromolar concentrations.¹³ Therefore, to nullify the detrimental effects

Received: December 30, 2023

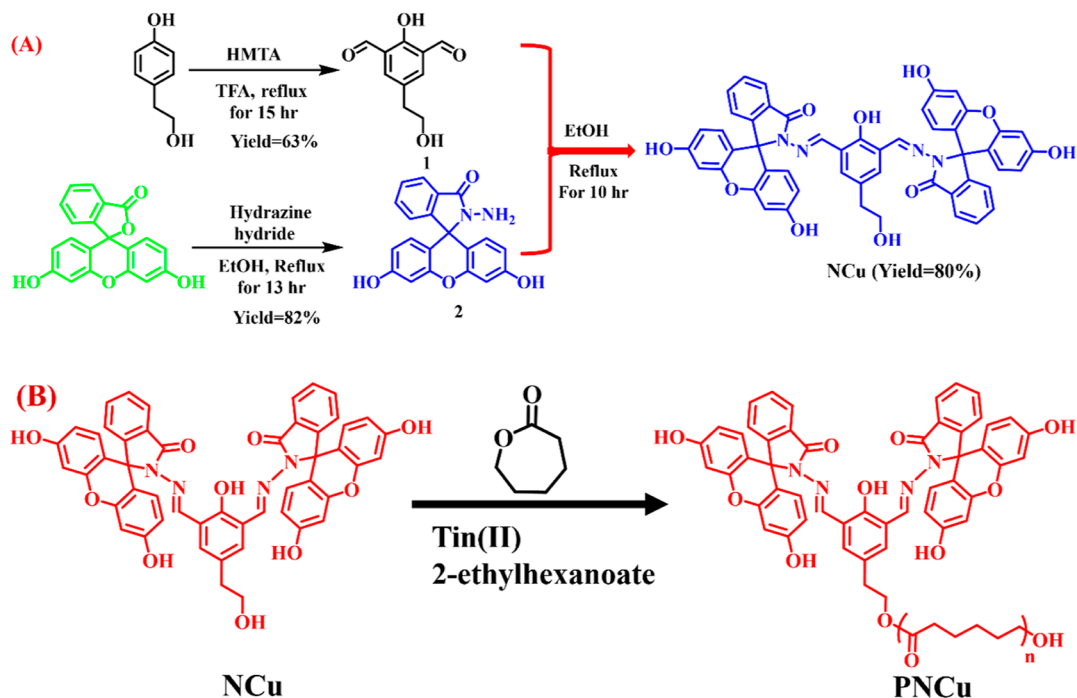
Revised: February 18, 2024

Accepted: February 21, 2024

Published: March 6, 2024



Scheme 1. (A) Synthetic Scheme for NCu and (B) PNCu



of Cu^{2+} ions for the sake of the environment and living organisms, we designed a sensor molecule that is not only able to detect Cu^{2+} ions but also remove them selectively from the water medium. Previously, several detection techniques have been reported in the literature for selective identification of Cu^{2+} ions, which include graphite furnace atomic absorption spectrometry, atomic absorption spectrometry, inductively coupled plasma emission spectrometry, electrochemical stripping analysis, voltammetry, spectrophotometry, and inductively coupled plasma mass spectrometry.^{14–20} Despite the high sensitivity of these instrumentation methods, their use has been limited due to their cost-effectiveness, high technicality, and instrument availability, which restricts their use. The replacement of the detection technique for Cu^{2+} ions by orthodox methods is the construction of chemical sensors proficient in showing instantaneous results in the presence of Cu^{2+} ions. Among different sensors, the colorimetric detection technique comprises a well-designed substitute that has the benefits of fieldwork applicability, cost-effectiveness, no need for a reference solution, size, bulky devices, and long processing time over the traditional analytically sophisticated instruments.^{21–23} So far, most of the reported colorimetric sensors are based on small molecules.²⁴ Being a small molecule, it has certain limitations and disadvantages, like sensitivity, real-time detection, and in-field applications, which restrict its application in a real field. Whereas polymer-based macromolecular sensors are preferred due to their distinctive nature of detection technique, novel side chain interaction, and excellent biocompatibility for in vivo study.^{25–29}

Also, according to the literature reports until now, where both sensing at the same time and removal of the Cu^{2+} ion at the same time take place together by using the polymer-based sensor macromolecule is rare.³⁰ This motivated us to develop a biodegradable caprolactone-based polymeric macromolecule for the selective and sensitive detection of Cu^{2+} ions and the removal of Cu^{2+} ions from water. The final monomer (NCu) was synthesized by a condensation reaction between

dialdehyde and the amine derivative of fluorescein (2), which further undergoes ring-opening polymerization in the presence of caprolactone to form our final polymer (PNCu). Here, we have incorporated the biodegradable polycaprolactone backbone to increase biodegradability and hydrophobicity so that the polymeric backbone can help to separate the Cu^{2+} ions from water. It was confirmed that both the monomer (NCu) and the polymer (PNCu) exhibited excellent LOD, which is quite below the limit stated by USEPA. In our experience, this is the first biodegradable, caprolactone-based polymeric sensor (PNCu) for selective and sensitive detection while also removing Cu^{2+} ions from water.

EXPERIMENTAL SECTION

We synthesized the final monomer by the condensation reaction between compound 1 and compound 2 via the formation of an imine bond on both sides of the molecule (Scheme 1A). Next, the formation of the NCu has been confirmed by ^1H , ^{13}C NMR spectroscopy, and mass spectrometry (Figures S4–S6). After that, the final polymer PNCu was synthesized with the help of a ring-opening polymerization technique in the presence of a caprolactone moiety with different feed ratios to get our desired polymer (Scheme 1B). After synthesizing the final polymer, we characterized them by ^1H NMR spectroscopy and gel permeable chromatography (Figures S7–S10). Detailed information regarding the targeting and incorporated caprolactone units within the polymer is given in Table S1. We have enlisted every synthetic detail related to our monomer and the polymer in the Supporting Information. In-depth solution preparation for spectroscopic analysis is discussed in Supporting Information and followed through all the experiments. All the detailed materials, sample preparation techniques, and spectroscopic data are listed in the Supporting Information.

RESULTS AND DISCUSSION

Photophysical Studies of NCu

After confirming the successful synthesis of NCu, we focused on the photophysical studies of the sensor. Initially, it was observed that NCu displayed an absorption maximum near

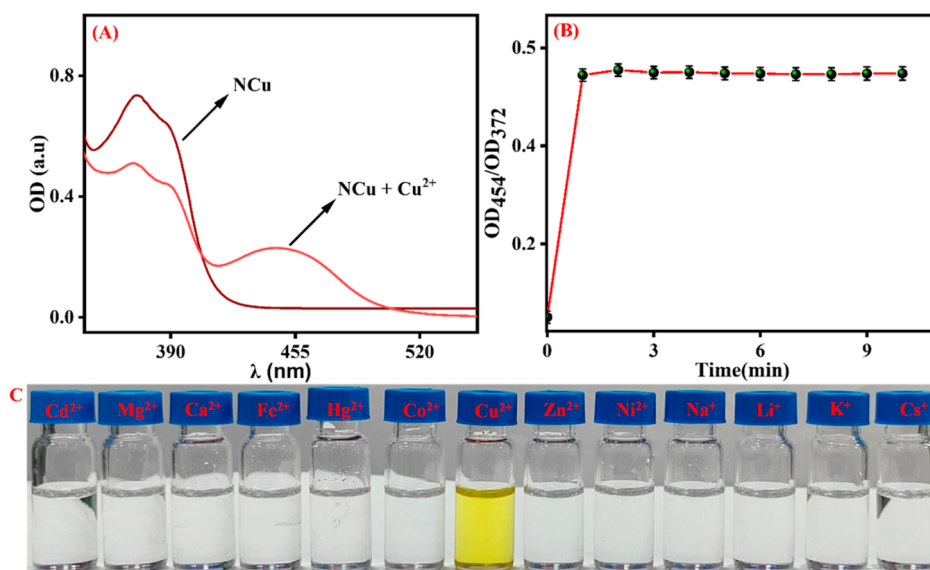


Figure 1. (A) UV–vis spectroscopic studies of NCu (100 μM) in the presence and absence of Cu^{2+} ions in DMSO–PBS buffer (8:2, v/v) medium. (B) Time-dependent study of NCu (100 μM) in the presence of Cu^{2+} ions (100 μM) in DMSO/PBS (8:2, v/v, pH-7.4) medium. (C) Selectivity studies of NCu (100 μM) in the presence of different metal ions in the naked eyes.

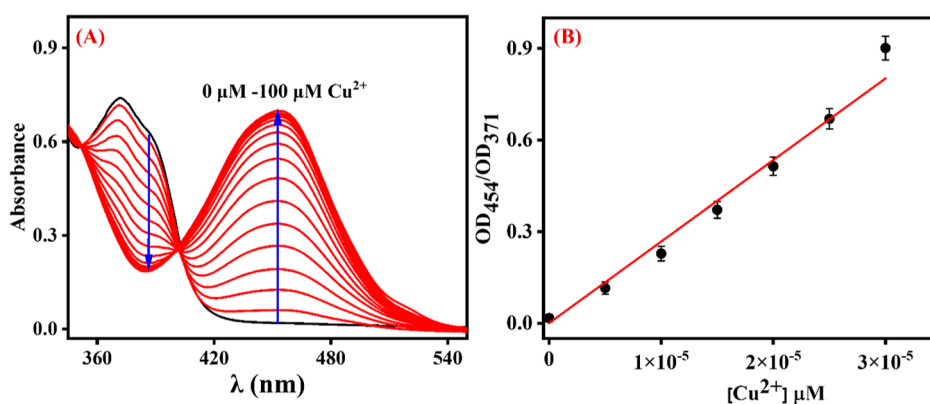


Figure 2. (A) UV–vis spectroscopic titration of NCu (100 μM) with the changing concentration of Cu^{2+} ions from 0 to 100 μM in DMSO–PBS buffer (8:2, v/v) medium (B) corresponding calibration curve of $\text{OD}_{454}/\text{OD}_{372}$ vs $[\text{Cu}^{2+}]$.

about 372 nm with a colorless solution in dimethyl sulfoxide (DMSO)/phosphate-buffered saline (PBS) (8:2, v/v, pH-7.4) medium. Whereas, upon the addition of the Cu^{2+} ion, a new absorption peak at 454 nm was observed along with a decrease in maxima at 372 nm (Figure 1A). This spectral change of NCu in UV–vis spectroscopy, accompanied by the change in color of the solution from colorless to yellow in the naked eye, could be due to the binding between the Cu^{2+} ions and the sensor molecule. Detection is a vital parameter of a sensor system to ensure its effectiveness. For that, we studied the time-dependent behavior of the NCu in the presence of Cu^{2+} ions in a DMSO/PBS (8:2, v/v, pH-7.4) medium. It was observed that the sensor molecule NCu displayed an instantaneous (within 1 min) change of the color of the solution from colorless to yellow after the addition of the Cu^{2+} ions, along with a new absorption maximum of a wavelength at 454 nm (Figure 1B). To check the stability of the color of the solution, we observed the solution over 2 days, and it was concluded that the color of the solution was stable for up to 2 days, which implies that the binding between the Cu^{2+} ions and NCu is very strong in the solution (Figure S17).

To inspect the selectivity properties of NCu, we performed UV–vis spectroscopic studies of NCu in the presence of different types of metal ions. According to our expectations, we observed a new absorption peak at 454 nm only in the presence of Cu^{2+} ions. Whereas in the case of the other metal ions, we did not find any such spectral changes (Figure S11A,B). Also, a change of color was noticed from colorless to yellow only in the case of Cu^{2+} ions over other metal ions, which implies that there is no interaction taking place for the other metal ions (Figure 1C). So far, from the UV–vis spectroscopic studies, it was confirmed that our sensor molecule NCu can detect Cu^{2+} ions selectively within 1 min over different types of other metal ions by changing the color from colorless to yellow along with a significant spectral change.

So far, the obtained excellent positive outcomes related to the time-dependent and selectivity studies of NCu encouraged us to study further in detail the sensitive behavior of NCu toward Cu^{2+} ions. Toward that, we did UV–vis titration of NCu with the gradual and progressive addition of Cu^{2+} ions from 0 to 100 μM (as mentioned in Figure 2A). As anticipated, with the gradual increase of the concentration of the Cu^{2+} ions,

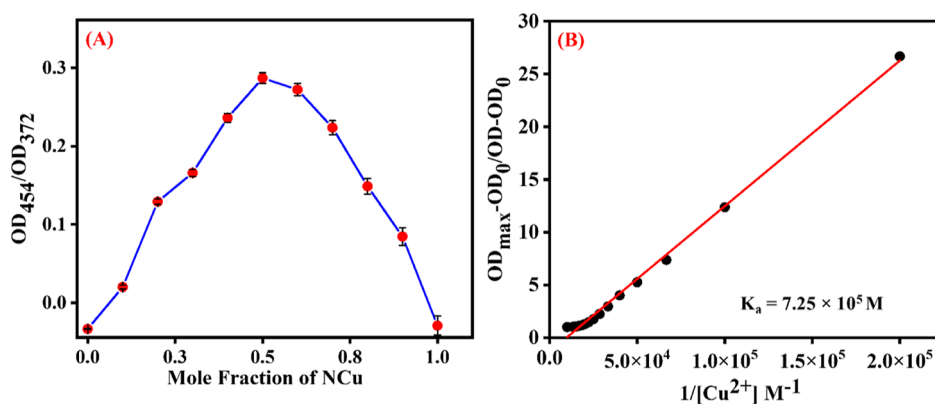


Figure 3. (A) Job's plot via the UV–vis spectroscopic technique to determine the binding ratio between NCu (50 μM) and Cu^{2+} ions (50 μM). (B) Benesi–Hildebrand plot from the UV–vis spectroscopic technique to calculate the binding constant.

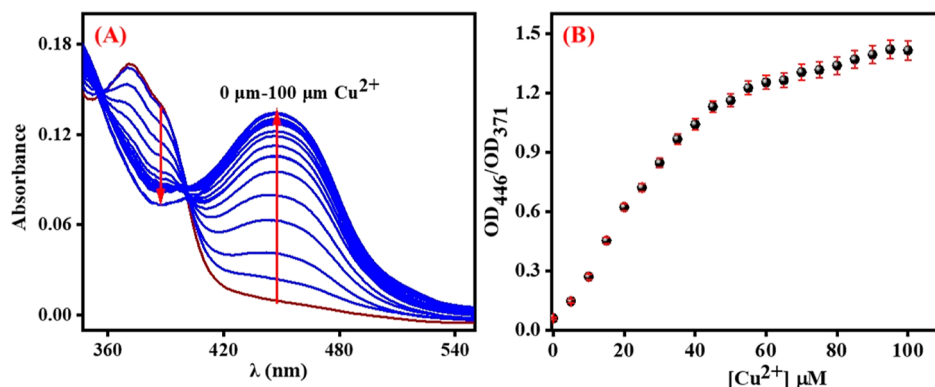


Figure 4. (A) UV–vis titration of PNCu-3 (100 μM) with increasing the concentration of Cu^{2+} ions from 0 to 100 μM in pure DMSO (B) Corresponding ratiometric curve of the $\text{OD}_{446}/\text{OD}_{371}$ vs $[\text{Cu}^{2+}]$.

the absorption maxima near about 372 nm decreased and the absorption maxima near about 454 nm increased in a ratiometric manner, ultimately achieving a plateau after the addition of 50 μM of Cu^{2+} ions (Figure S12). Admirable linearity with $R^2 = 0.98522$ was noticed with the gradual elevation of absorption intensity at 454 nm with varying concentrations of Cu^{2+} ions (0–30 μM), as shown in Figure 2B and Table S2. With the help of the linearity curve, we calculated the limit of detection of the Cu^{2+} ions. It was found that the obtained LOD value is 29 nM, which is quite lower than the limit permitted by WHO. All these above-discussed results confirmed the excellent selectivity and sensitivity of NCu toward Cu^{2+} ions. In this respect, we were curious enough to check the effect of the pH on NCu. For this purpose, we carried out UV–vis spectroscopic studies of NCu with varying pH in the absence and presence of Cu^{2+} ions. The pH-dependent studies revealed that the spectral behavior of NCu remains silent in the absence of Cu^{2+} ions with a change in pH. Whereas, in the presence of Cu^{2+} ions, the absorption intensity at 454 nm gradually increases with increasing pH up to 6, and after that, it becomes almost saturated (Figure S13). The obtained data from the pH-dependent study imply that NCu can be very efficient in working in the physiological pH range.

Determination of the Binding Constant and Stoichiometry

So far from the UV–vis spectroscopic studies, we explored the sensor molecule NCu interact with the Cu^{2+} ions instantaneously by changing the color of the solution from colorless to yellow with high selectivity and sensitivity. To understand this

binding stoichiometry, we performed the Job's plot experiment using UV–vis spectroscopic techniques. Therefore, we did the absorption studies by varying the mole fraction of the Cu^{2+} ions (Figure 3A) on the sensor NCu. From this plot, we determined that NCu is binding with the Cu^{2+} ions in a 1:1 ratio. Also, we calculated the association constant from the titration experiment, which turned out to be $7.25 \times 10^5 \text{ M}$ by using the Benesi–Hildebrand equation (Figure 3B).

Photophysical Behavior of the PNCu

So far from the above studies, we have come to know that our sensor molecule, NCu, can detect the presence of Cu^{2+} ions with excellent selectivity and sensitivity. But the monomer NCu failed to separate out the Cu^{2+} ions from the solution. To counter this problem, we have synthesized caprolactone-based biodegradable polymer (PNCu) with the help of the ring-opening polymerization method for the detection as well as the separation of the Cu^{2+} ions from the solutions. Toward this goal, we made three different polymers with different caprolactone ratios (PNCu-1, PNCu-2, and PNCu-3) and three different average molecular weights of 2000, 2400, and 4200 Da with PDI values of 1.08, 1.02, and 1.05 (Figure S10 and Table S1), respectively. We performed all of the photophysical studies (sensing properties) by using PNCu-3. To understand the sensing behavior of the PNCu-3, we first checked the time-dependent studies of the PNCu-3 with the addition of Cu^{2+} ions. It turned out that, like NCu, PNCu-3 also instantaneously detected the Cu^{2+} ions within 1 min by changing the color from colorless to yellow in the naked eye at a wavelength of 446 nm. After getting an excellent response in

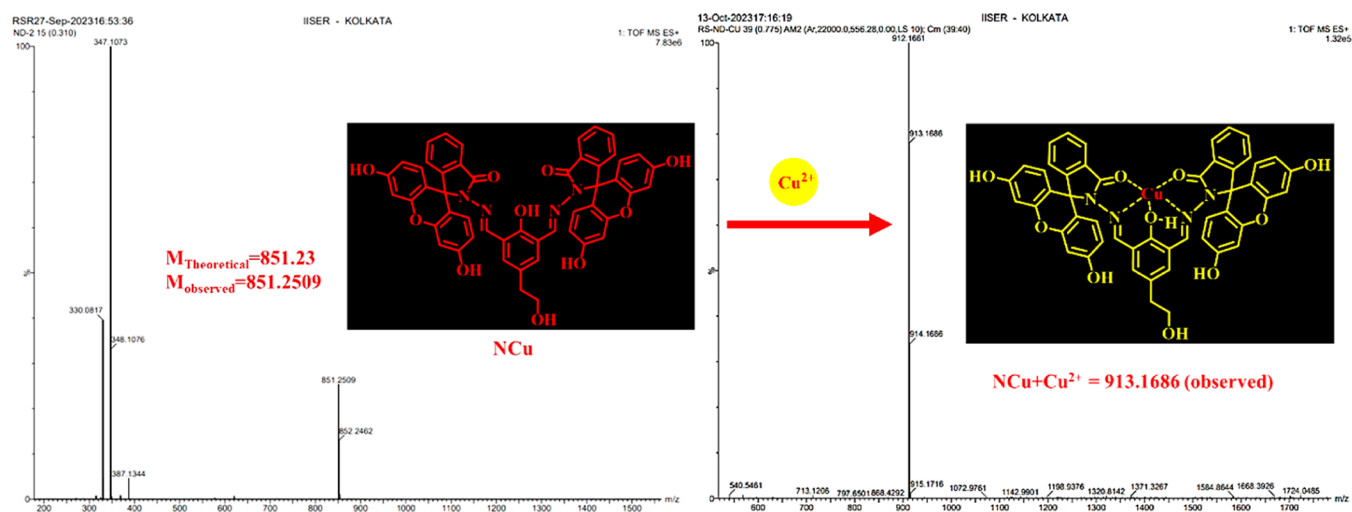


Figure 5. Mass spectrometry titration of NCu in the presence of Cu^{2+} ions.

the time dependent study, which motivated us to check the sensitivity of the PNCu-3 in the presence of Cu^{2+} ions. For that purpose, we did the UV–vis titration of the PNCu-3 by increasing the concentration of the Cu^{2+} ions from 0 to 100 μM (as mentioned in Figure 4A). It was observed that with the addition of Cu^{2+} ions, the absorption maxima at 371 nm gradually decreased and the absorption maxima at 446 nm slowly increased; ultimately, a plateau was attained after the addition of 60 μM of Cu^{2+} ions (Figure 4B). Estimable linearity with $R^2 = 0.99213$ was recorded with the gradual advancement of absorption intensity at 446 nm with changing the concentration of Cu^{2+} ions (0–50 μM) as shown in Figure S14 and Table S3. From this linearity curve, we determined that the limit of detection of Cu^{2+} ion for PNCu-3 is 0.3 μM , which is much less than the limit permitted by WHO.

Study of the Sensing Mechanism

We have predicted the binding mechanism of Cu^{2+} with NCu using Job's plot and mass spectroscopic techniques. As per Job's plot experiment, we predicted the 1:1 binding stoichiometry between the sensor and Cu^{2+} ions. Two spirolactam rings contain fluorescein units, and the $-\text{OH}$ group of the phenyl ring appears to be an excellent binding cavity for the copper ion. As we know, N and O atoms are good for binding Cu^{2+} ions due to the electronegativity difference. The nitrogen of the $\text{C}=\text{N}$ groups, the oxygen atom of the $\text{C}=\text{O}$ groups, and the $-\text{OH}$ group bind with the Cu^{2+} ion to produce a charge transfer complex, and thus we observed a yellow color after binding. Ideal interaction and proper cavity size in NCu are the reasons behind the selectivity toward copper. To confirm our hypothesis, we performed mass spectrometry of NCu in the presence of Cu^{2+} ions with 1:1 stoichiometry. From the obtained mass spectrometry data in Figure 5, we found a new peak at 913.1686 in the presence of the Cu^{2+} ions, which is exactly matching to the molecular weight of NCu binding with Cu^{2+} ions in a 1:1 ratio. So, from the mass spectrometry data, we can conclude the 1:1 binding between NCu and the Cu^{2+} ion.

DFT Calculation

To support and understand the sensing mechanism, we performed density functional theory (DFT) calculations in the monomeric unit. We first optimized the structure for the NCu and its complex with Cu^{2+} ions. From there, we produced

the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of NCu and its Cu^{2+} complexes Cu^{2+} ions. Also, we calculated the energies of the HOMO and LUMO of NCu and its complex with Cu^{2+} ions. It was observed that the difference in energy gap between the HOMO and the LUMO of the NCu is 3.14 eV, while upon complexation with one unit of Cu^{2+} ions, the energy gap reduces to 1.57 eV, which implies that it attains a more stabilized structure due to strong complex formation (as mentioned in Figure 6). These DFT calculations again affirm the experimental findings that one Cu^{2+} ion is bound with one NCu in a 1:1 ratio.

Real Sample Analysis

The outstanding results obtained from the selectivity and sensitivity studies of NCu and PNCu motivated us to further check the capability of PNCu-3 in the real system for the identification of Cu^{2+} ions. Initially, the UV–vis titration was carried out in the presence of PNCu-3 (50 μM) in pure water by changing the concentration of the Cu^{2+} ions from 5 to 45 μM , and the linear plot of $\text{OD}_{446}/\text{OD}_{371}$ vs $[\text{Cu}^{2+}]$ was derived with excellent linearity and an R^2 value of 0.99671 (as mentioned in Figure S15). This linear plot will be utilized as a calibration curve to determine the unknown concentration of Cu^{2+} ions present in the real sample. To check the in-field application of PNCu-3, we collected the pond water from the IISER-k pond and spiked it with different concentrations of the Cu^{2+} ions along with PNCu-3 (50 μM). Now, from the UV–vis spectroscopic study, we got absorption maxima with different $\text{OD}_{446}/\text{OD}_{371}$ values, which we put in the calibration curve to get the actual concentration of the Cu^{2+} ions present in the solution. After that, we calculated the percentage of the recovery with the assistance of a calibration curve (Figure S15). It was observed that in all the cases, the percentage of recovery was more than 95% (as mentioned in Table S4). The higher recovery suggested that PNCu-3 can be utilized for sensing Cu^{2+} ions in real samples.

Study for the Separation of the Cu^{2+} Ions from the Water Solution

Till now, the obtained data can point out that PNCu-3 has a high potential to detect the Cu^{2+} ions selectively and sensitively with a lower LOD, which motivated us to further check whether it can separate Cu^{2+} from the aqueous solutions

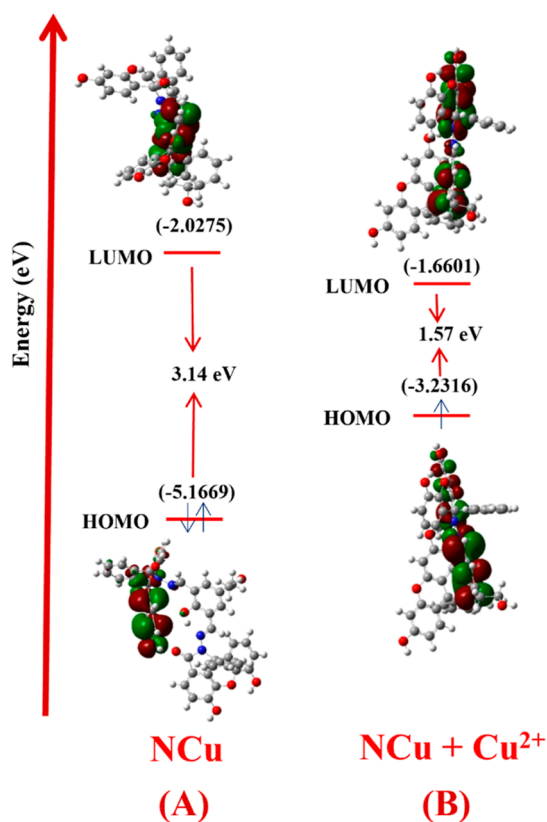


Figure 6. HOMO–LUMO plot of the monomeric units of (A) NCu and (B) NCu + Cu²⁺.

or not. For that reason, we did the ring-opening polymerization of NCu with caprolactone in the presence of the tin(II) 2-ethylhexanoate catalyst. We hypothesized that increasing the hydrophobicity within the NCu via polymerization would help to separate the Cu²⁺ from the water medium through the binding mechanism, as mentioned in Figure 5. Here, we synthesized three different sets of polymers with varying three different caprolactone ratios to vary the hydrophobicity within in the polymer. After that, we did the solvent-dependent studies of each polymer by varying the DMSO and water (v/v) in the presence of the Cu²⁺ ions. Interestingly, we observed that with increasing the percentage of water, the absorption maxima at 446 nm decreased, and at a 9:1 water-to-DMSO ratio, it showed very negligible absorption maxima at 446 nm

in the presence of Cu²⁺ ions along with yellow color precipitation (Figure 7A). Also, it was noticed that increasing the caprolactone unit in the polymer would decrease the absorption maximum at 446 nm (Figure 7A) and that it would start to precipitate out of the solutions.

From the solvent-dependent study of the three polymers, it was confirmed that PNCu-3 is showing negligible absorption maxima at 446 nm and a higher precipitate in the presence of Cu²⁺ ions in the 9:1 water and DMSO mixture. That is why we picked PNCu-3 as a better member for the separation study of Cu²⁺ ions. To separate the copper from water, in a known concentration of copper solution in water, we added PNCu-3 and stirred the solution for 2 h. After that, we separate the yellow precipitate and the colorless filtrate separately. To check whether this precipitate contained Cu²⁺ ions or not, we did two separate UV–vis spectroscopic studies of the precipitate by dissolving it in DMSO and a colorless filtrate. It was observed that the filtrate showed no absorption maxima at 446 nm. On the other hand, the precipitate was showing a new absorption peak at 446 nm, which proves that the precipitates contain Cu²⁺ ions, which are responsible for the new absorption maxima (Figure 7B). Also, to know the composition of the precipitate, we did an energy dispersive X-ray (EDX) analysis of the precipitate (Figure S16). From the edax experiment, we found that the precipitate contains Cu²⁺ ions. So, the UV–vis absorption study of the precipitate and the EDX study prove that the precipitate contains Cu²⁺ ions. Hence, we can say that our polymer PNCu-3 can separate copper from water.

CONCLUSIONS

We successfully synthesized the fluorescein-based monomer NCu and its caprolactone-based biodegradable polymer PNCu through ring-opening polymerization. The NCu has been utilized for the ultrafast, selective, and sensitive detection of the Cu²⁺ ions by changing the color of the solution from colorless to yellow, with the lowest limit of detection of 29 nM. From the mass titration and Job's plot, it was established that the NCu is binding with the Cu²⁺ ions in a 1:1 ratio, which was further supported by the DFT calculation study. In the case of the polymer PNCu, it is not only able to detect the Cu²⁺ ions but is also able to separate the Cu²⁺ ions from the water solution. The incorporation of the caprolactone unit assisted in separating the Cu²⁺ ions by binding with Cu²⁺ ions present in the solution by increasing the hydrophobicity, which helps the polymer precipitate out of the solution after binding with the

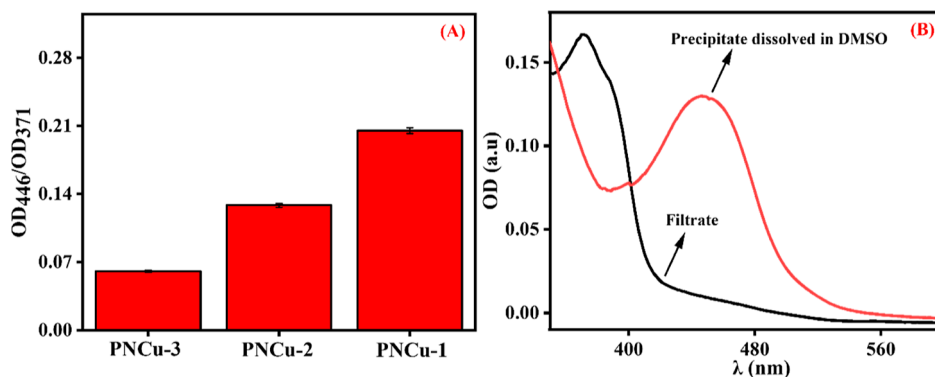


Figure 7. (A) UV–vis spectroscopic study of PNCu-1, PNCu-2, and PNCu-3 in the presence of Cu²⁺ ions. (B) UV–vis spectroscopic study of PNCu-3 in both filtrate and precipitate.

Cu²⁺ ions. Also, we checked the applicability of PNCu in the real system to detect the Cu²⁺ ions in the real system. It was observed that, along with PNCu, it has a high capability to detect Cu²⁺ ions in real environments. To our knowledge, we believe that this is the first biodegradable caprolactone-based polymeric system that can detect and, at the same time, separate the Cu²⁺ ions from the water solution.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acspolymersau.3c00056>.

Materials, methods, sample preparation technique, synthesis and characterization of NCu and PNCu, GPC data of PNCu, UV–vis spectroscopic study of NCu and PNCu, and EDX study (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Raja Shunmugam – Polymer Research Centre, Department of Chemical Sciences, Indian Institute of Science Education and Research—Kolkata, Kolkata, West Bengal 741246, India; orcid.org/0000-0002-0221-127X; Email: sraja@iiserkol.ac.in

Authors

Narayan Das – Polymer Research Centre, Department of Chemical Sciences, Indian Institute of Science Education and Research—Kolkata, Kolkata, West Bengal 741246, India

Tapendu Samanta – Polymer Research Centre, Department of Chemical Sciences, Indian Institute of Science Education and Research—Kolkata, Kolkata, West Bengal 741246, India; orcid.org/0000-0002-8542-275X

Srishti Gautam – Polymer Research Centre, Department of Chemical Sciences, Indian Institute of Science Education and Research—Kolkata, Kolkata, West Bengal 741246, India

Karina Khan – Polymer Research Centre, Department of Chemical Sciences, Indian Institute of Science Education and Research—Kolkata, Kolkata, West Bengal 741246, India

Susmita Roy – Polymer Research Centre, Department of Chemical Sciences, Indian Institute of Science Education and Research—Kolkata, Kolkata, West Bengal 741246, India; orcid.org/0000-0001-6411-4347

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acspolymersau.3c00056>

Author Contributions

N.D. First author. N.D. synthesized both the monomer and the polymer, did all the photophysical studies, drew all the figures, and wrote the manuscript. T.S. helped write the manuscript. Srishti helped synthesize the monomer. Karina did all the DFT calculations under Dr. Susmita Roy's supervision. R.S. monitored and supervised every step of this project. CRediT: Srishti Gautam methodology; Karina Khan data curation; Raja Shunmugam supervision.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge IISER-Kolkata for the research facility and infrastructure. N.D. acknowledges UGC for fellowship. R.S. acknowledges the Ministry of Textiles for the funding.

■ ABBREVIATIONS

NCu, final monomer; PNCu, final polymer

■ REFERENCES

- (1) He, Z. L.; Yang, X. E.; Stoffella, P. J. Trace elements in agroecosystems and impacts on the environment. *J. Trace Elem. Med. Biol.* **2005**, *19*, 125–140.
- (2) Gupta, M.; Balamurugan, A.; Lee, H. i. Azoaniline-based rapid and selective dual sensor for copper and fluoride ions with two distinct output modes of detection. *Sens. Actuators, B* **2015**, *211*, 531–536.
- (3) Herawati, N.; Suzuki, S.; Hayashi, K.; Rivai, I. F.; Rivai, F. I.; Koyama, H. Cadmium, copper and zinc levels in rice and soil of Japan, Indonesia and China by soil type. *Bull. Environ. Contam. Toxicol.* **2000**, *64*, 33–39.
- (4) Shallari, S.; Schwartz, C.; Hasako, A.; Morel, L. J. Heavy metals in soils and plants of serpentine and industrial sites of Albania. *Sci. Total Environ.* **1998**, *209*, 133–142.
- (5) Nriagu, J. O. A global assessment of natural sources of atmospheric trace metals. *Nature* **1989**, *338*, 47–49.
- (6) Arruti, A.; Fernández-Olmo, I.; Irabien, A. Evaluation of the contribution of local sources to trace metals levels in urban PM_{2.5} and PM₁₀ in the Cantabria region (Northern Spain). *J. Environ. Monit.* **2010**, *12* (7), 1451–1458.
- (7) Sträter, E.; Westbeld, A.; Klemm, O. Pollution in coastal fog at Alto Patache, Northern Chile. *Environ. Sci. Pollut. Res. Int.* **2010**, *17* (9), 1563–1573.
- (8) Pacyna, J. M. Monitoring and assessment of metal contaminants in the air. *Toxicology of Metals*; CRC Press: Boca Raton, 1996; pp 19–28.
- (9) Wang, Z.; Wang, M.; Wu, G.; Wu, D.; Wu, A. Colorimetric detection of copper and efficient removal of heavy metal ions from water by diamine-functionalized SBA-15. *Dalton Trans.* **2014**, *43*, 8461–8468.
- (10) Butter, E.; Greenwood, N. N.; Earnshaw, A. N. N. Greenwood, A. Earnshaw: Chemistry of the elements. Pergamon press oxford 1984, 1542 seiten, 7 anhänge Preis: US \$ 34.95. ISBN 0–08–022057–6. *Cryst. Res. Technol.* **1985**, *20*, 662.
- (11) Chandra, R.; Ghorai, A.; Patra, G. K. A simple benzildihydrazone derived colorimetric and fluorescent ‘on–off–on’ sensor for sequential detection of copper (II) and cyanide ions in aqueous solution. *Sens. Actuators, B* **2018**, *255*, 701–711.
- (12) Na, Y. J.; Choi, Y. W.; Yun, J. Y.; Park, K. M.; Chang, P. S.; Kim, C. Dual-channel detection of Cu²⁺ and F[–] with a simple Schiff-based colorimetric and fluorescent sensor. *Spectrochim. Acta, Part A* **2015**, *136*, 1649–1657.
- (13) Zheng, Y.; Orbulescu, J.; Ji, X.; Andreopoulos, F. M.; Pham, S. M.; Leblanc, R. M. Development of Fluorescent Film Sensors for the Detection of Divalent Copper. *J. Am. Chem. Soc.* **2003**, *125*, 2680–2686.
- (14) De Silva, A. P.; Fox, B. D.; Huxley, M. J. A.; Moody, S. T. Combining luminescence, coordination, and electron transfer for signaling purposes. *Coord. Chem. Rev.* **2000**, *205*, 41.
- (15) Cebrian, E.; Agell, G.; Martí, R.; Uriz, M. Response of the Mediterranean sponge *Chondrosiareniformis* Nardo to copper pollution. *Environ. Pollut.* **2006**, *141*, 452–458.
- (16) Anthemidis, A.; Zachariadis, G.; Stratis, J. On-line preconcentration and determination of copper, lead, and chromium(VI) using unloaded polyurethane foam packed column by flame atomic absorption spectrometry in natural waters and biological samples. *Talanta* **2002**, *58*, 831–840.

(17) Bispo, M. S.; Korn, M. d. G. A.; Morte, E. S. d. B.; Teixeira, L. S. G. Determination of lead in seawater by inductively coupled plasma optical emission spectrometry after separation and pre-concentration with cocrystallized naphthalene alizarin. *Spectrochim. Acta, Part B* **2002**, *57*, 2175–2180.

(18) Li, J.; Lu, F.; Umemura, T.; Tsunoda, K. Determination of lead by hydride generation inductively coupled plasma mass spectrometry. *Anal. Chim. Acta* **2000**, *419*, 65–72.

(19) Fang, G.; Meng, S.; Zhang, G.; Pan, J. Spectrophotometric determination of lead in foods with dibromo-p-methyl-bromosulfonazo. *Talanta* **2001**, *54*, 585–589.

(20) Arancibia, V.; Nagles, E.; Cornejo, S. Determination of lead in the presence of morin-5'-sulfonic acid and sodium dodecyl sulfate by adsorptive stripping voltammetry. *Talanta* **2009**, *80*, 184–188.

(21) Liu, J.; Yu, M.; Wang, X. C.; Zhang, Z. A highly selective colorimetric sensor for Hg²⁺ based on nitrophenyl-aminothiourea. *Spectrochim. Acta, Part A* **2012**, *93*, 245–249.

(22) Yagi, S.; Nakamura, S.; Watanabe, D.; Nakazumi, H. Colorimetric sensing of metal ions by bis(spiropyran) podands: Towards naked-eye detection of alkaline earth metal ions. *Dyes Pigm.* **2009**, *80*, 98–105.

(23) You, J. M.; Jeong, H.; Seo, H.; Jeon, S. A new fluoride ion colorimetric sensor based on dipyrrolemethanes. *Sens. Actuators, B* **2010**, *146*, 160–164.

(24) Goshisht, M. K.; Patra, G. K.; Tripathi, N. Fluorescent Schiff base sensors as a versatile tool for metal ion detection: strategies, mechanistic insights, and applications. *Mater. Adv.* **2022**, *3*, 2612–2669.

(25) Samanta, T.; Das, N.; Patra, D.; Kumar, P.; Sharmistha, B.; Shunmugam, R. Reaction-Triggered ESIPT Active Water-Soluble Polymeric Probe for Potential Detection of Hg²⁺/CH₃Hg⁺ in Both Environmental and Biological Systems. *ACS Sustain. Chem. Eng.* **2021**, *9* (14), 5196–5203.

(26) Samanta, T.; Das, N.; Shunmugam, R. Intramolecular Charge Transfer-Based Rapid Colorimetric In-Field Fluoride Ion Sensors. *ACS Sustain. Chem. Eng.* **2021**, *9* (30), 10176–10183.

(27) Samanta, T.; Das, N.; Singha, J.; Shunmugam, R. Unusual red-orange emission from rhodamine-derived polynorbornene for selective binding to Fe³⁺ ions in an aqueous environment. *Anal. Methods* **2020**, *12*, 4159–4165.

(28) Singha, J.; Das, N.; Shunmugam, R. Nanomolar detection of hypochlorite in ground water samples by a norbornene-based polymeric sensor via unusual fluorescence turn-on response. *J. Macromol. Sci., Pure Appl. Chem.* **2023**, *60*, 751–763.

(29) Sharma, R.; N Chavan, S.; Lee, H. Fluorescent imidazolium hydrogels for tracing and recovering platinum with highest purity from spent auto catalyst. *Sens. Actuators, B* **2023**, *396*, 134625.

(30) Choudhury, N.; Ruidas, B.; Saha, B.; Srikanth, K.; Das Mukhopadhyay, C.; De, P. Multifunctional tryptophan-based fluorescent polymeric probes for sensing, bioimaging and removal of Cu²⁺ and Hg²⁺ ions. *Polym. Chem.* **2020**, *11*, 2015–2026.