



# Synthesis of Polynorbornene Based Molecular Self-assembly for the Detection of Copper Ions Present in the Environmental Water Samples

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## ABSTRACT

Metal-assisted molecular self-assembly finds applications in optoelectronics, chemical sensing and catalysis. In this article, fluorescein based polynorbornene is synthesized and its molecular self-assembly is used to detect the presence of copper(II) ions in environmental water samples (pond waters). First of all, the sequential procedures of the synthesis of norbornene and polynorbornene are accomplished using simple organic compounds available in the Indian market. Various intermediate compounds and norbornene are characterized by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR techniques. Structure of polynorbornene is proved by  $^1\text{H}$  NMR spectroscopy. Molecular weight of polynorbornene is obtained using Acquity advanced polymer chromatography. Particle size of polymer nano-aggregates is derived by using FESEM microscope. This polynorbornene (PNor-Flu) is used for the selective and sensitive detection of the copper(II) ions with an excellent LOD of  $0.27\ \mu\text{M}$ , far below the limit decided by the Environmental Protection Agency (EPA) of USA. This is achieved with the help of UV-Vis studies and spectroscopic titrations using OD416/OD350. As far the self-assembly is concerned using microscopic analysis, polynorbornene with a higher number of hydroxyl groups shows rod-like self-assembly. Polynorbornene structure is again transformed to a spherical shape in the presence of the copper(II) ions even in micromolar concentration. From this change, it is believed that the polynorbornene has a high potentiality for sensing the copper(II) ions, which helps it to impart unique morphological properties. From the tests performed on real water samples, polynorbornene has proved its high efficiency of selective and sensitive detection power for detecting copper(II) ions in pond waters.

**Keywords:** Polymer, Fluorescein, Polynorbornene, Molecular Self-assembly, Sensing.

## INTRODUCTION

Nature organized itself with a wide variety of molecular architecture with different types of nanostructural self-assembly which includes DNA double helix, tubulin assembly lipid build blocks,

etc. Molecular self-assembly is a highly efficient process that involves non-covalent interactions such as hydrogen bonding, hydrophobic forces,  $\pi$ -stacking interactions, van der Waals forces, metal coordination, and electrostatic interactions. These forces help in transforming a disordered system into



an ordered one, with well-organized shapes, sizes, and dimensions<sup>1</sup>. Molecular self-assembly assists in the spontaneous association of the macromolecules to adopt dynamic supramolecular assemblies such as nanofibers, nanoparticles, and nanotubes. By connecting the unique properties of host-guest with molecular self-assembly, it is possible to unlock new frontiers in optoelectronics, sensing, and catalysis. This simple and efficient approach offers tremendous potential for advancing cutting-edge technologies and solving complex scientific challenges. In this article, it is proposed to make a polymer-based metal-assisted molecular self-assembly. Its sensing properties have enough potential for real-life application in the sensing area<sup>2-5</sup>. Heavy metals, particularly copper(II) ions, are crucial for the metabolism of living organisms<sup>6</sup>. Copper (II) ions serve as a cofactor for cuproenzymes and help regulate various metabolic processes in our bodies, including neuro-signal transduction and gene expression<sup>7</sup>. This highlights the importance of copper(II) ions in maintaining optimal physiological functions. Excessive intake of copper can be extremely harmful to our health as it is highly toxic and can result in various health complications such as liver function abnormalities, liver cirrhosis, or Wilson's disease. Industries that use copper without proper regulation can lead to contamination of environmental water, and it can ultimately enter our bodies through the food chain<sup>8</sup>. Therefore, it is important to detect and monitor Cu<sup>2+</sup> ions in water or other aqueous solutions to ensure environmental safety and promote good health. Numerous methods have been reported in the scientific literature for detecting and monitoring the presence of copper(II) ions in water. Most of these methods involve electromagnetic or mass spectroscopy techniques such as ICP-MS, ICP-OES, atomic absorption spectrometry, laser-induced breakdown spectroscopy, voltammetric techniques, and atomic emission spectrometry<sup>9</sup>. However, the major drawback of these techniques is that they require expensive equipment and difficult sample preparation procedures, which makes them less widely available and restricts their application for detection of copper. On the other hand, colorimetric sensors derived from polymers are in high demand due to their unique self-assembly based on host-guest interaction<sup>10,11</sup>. They are also very economical and easily accessible for detecting copper ions. Our present work represents a new sensor for the detection of copper ions from environmental samples. A fluorescein-derived norbornene-based monomer, Nor-Flu, and its

polymer, PNor-Flu, are introduced in this article. These compounds demonstrate exceptional selectivity and sensitivity for copper ions detection. With this new work, it is possible to detect copper ions with greater accuracy and efficiency, making it a highly valuable tool for environmental monitoring and analysis. It was previously reported that copper has a higher affinity to make coordination bonds with the electronegative nitrogen atom of the imine bond and oxygen atom of the hydroxyl group which presents very adjacently to make a stable complex along with color change of the solution in the presence of the copper due to the formation of the highly stable ligand to metal charge transfer complex. It was confirmed that both the monomer (Nor-Flu) and the polymer (PNor-Flu) exhibited excellent LOD which is quite below the limit stated by US-EPA. Also in the case of the polymer due to the presence of amphiphilicity within the polymeric macromolecules, it is showing interesting host-guest molecular self-assembly in the presence and the absence of the copper ions with unique molecular architecture.

## MATERIALS AND METHODS

### Chemicals

Organic chemicals such as cis-5-norbornene-exo-2, 3-dicarboxylic anhydride, 4-aminophenol, Acetic acid, Hexamethelene diamine, Trifluoroacetic acid, Fluorescein, Hydrazine hydrate, Ethanol, Grubb's 2<sup>nd</sup> generation Grubbs catalyst, Ethyl vinyl ether, Dimethyl sulfoxide, Dichloromethane, Diethyl ether (Et<sub>2</sub>O), CDCl<sub>3</sub>, DMSO-d<sub>6</sub>, Sodium Hypochlorite, Hydrogen peroxide, and Tertiary butyl hydroperoxide are bought from Sigma Aldrich, Spectrochem, and Combiblocks. The stock analyte solutions of CuSO<sub>4</sub>, MgCl<sub>2</sub>, FeSO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, PbNO<sub>3</sub>, AgNO<sub>3</sub>, NiCl<sub>2</sub>, CdSO<sub>4</sub>, CaSO<sub>4</sub>, and AlCl<sub>3</sub> were prepared by using analar chemicals.

### Analysis

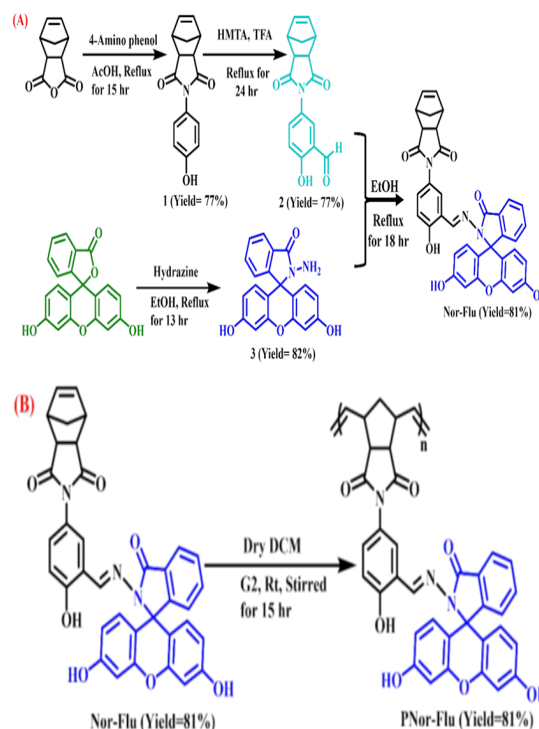
NMR characterizations were performed on a Bruker 500MHz instrument for both <sup>13</sup>C and <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopic techniques, employing DMSO-D<sub>6</sub> and CDCl<sub>3</sub> as the NMR solvents. Throughout the experiments, Tetramethylsilane served as the internal standard for calibration. Acquity Advanced Polymer Chromatography was used to get the molecular weight of the polymer with Omnisec Reveal detector, employing refractive index (RI), light scattering (RALS 90°, LALS 7° angle), and a viscometer for detection.

UV-Visible absorption studies were performed using a Perkin-Elmer Lambda 35 UV-Vis spectrometer, with a scan rate of 480nm/minute. Each absorption spectrum was measured individually in a 1 cm quartz cell for every solution. Sample preparation for UV-Vis studies were done with utmost care. All stock solutions of Nor-Flu and PNor-Flu were initially prepared in DMSO and later diluted with water for various experiments. Metal solutions were exclusively prepared in water. UV-Vis spectroscopy involved maintaining fixed concentrations of Nor-Flu ( $\mu\text{M}$ ) and PNor-Flu ( $\mu\text{M}$ ). Spectroscopic titrations were conducted by introducing fixed concentrations of Nor-Flu solution to successive increasing concentrations of  $\text{Cu}^{2+}$  ions. Real samples were consistently prepared using water as the solvent. Scanning electron microscope (SEM) was employed the high-performance variable pressure FE-SEM (Zeiss SUPRA 55VP-Field Emission Scanning Electron Microscope) to determine the size of the nano-aggregates. This FESEM utilizes patented GEMINI column technology and a Schottky type field emitter system, with a single condenser featuring a crossover-free beam path. In high vacuum mode, the resolution is 1.0nm at 15 kV and 1.6nm at 1 kV, while in variable pressure mode, it is 2.0nm at 30 kV.

## Synthesis

Though synthesis of polynorbornene (PNor-Flu) is not main objective of the research article, the synthetic methodology is shown in Scheme 1. The equential procedures of synthesis of polynorbornene is done using simple organic compounds available in the Indian market. Synthesis of the compounds 1-3, Nor-Flu and PNor-Flu involves synthetic procedures as detailed below. Synthesis of Compound-1 was synthesized first from analar chemicals. Cis-5-Norbornene-exo-2,3-dicarboxylic anhydride (1 g, 0.006 mol) was taken in a 100 mL roundbottom flask followed by the addition of glacial acetic acid. The mixture was stirred for 15 minutes. To the mixture 4-aminophenol (0.665 g, 0.006 mol) was added and refluxed at 110°C for 24 hours. After completion of the reaction, the mixture was cooled to room temperature. The formed precipitate was filtered and recrystallized from ethanol to obtain Compound 1 as brown solid (1.2 g, 77%). Synthesis of Compound-2 was synthesized from Compound 1. First Compound 1 (1 g, 0.004 mol) was taken in a 250 mL round-bottom flask and 50 mL of TFA added to it. After complete solubility of Compound 1, HMTA

(660 mg, 0.0048 mol) was added to the reaction mixture and kept in refluxing condition for 24 hours. After completion of the reaction, the mixture was cooled to room temperature. The cooled reaction mixture was transferred to a 250 mL separating funnel with DCM and extracted with 2(N) HCl solution, water, and brine. Then combined DCM layer was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure to obtain the crude product. Flash column chromatography was carried out t:o obtain Compound 2 as a white powder (700 mg, 64%). Synthesis of Compound 3 was synthesized from Compound 2. First Compound 2 (500 mg, 0.0018 mol) was dissolved in DMF and  $\text{K}_2\text{CO}_3$  (300 mg, 0.0022 mol) was added to it. The reaction mixture was stirred for 5 min followed by the addition of ethyl iodide (280 mg, 0.0018 mol). The overall mixture was stirred for 24 h at room temperature and the progress of the reaction was monitored using TLC. After completion of the reaction, the mixture was poured into ice-cold water. A white-colored precipitate was observed, which was filtered and washed with cold water to remove unreacted compounds. After drying, Compound 3 was obtained as a white-colored powder (490 mg, 90%). Compounds 1-3 were characterized using  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectral techniques<sup>12-17</sup>.



**Scheme 1(A). Synthetic scheme for Nor-Flu**

**(B) Synthetic scheme for PNor-Flu**

Synthesis of monomer Nor-Flu was obtained from Compounds 2&3. In a 100 mL round-bottom flask, 732 mg (2.116 mmol) of Compound 3 was dissolved in 5 mL of ethanol with the assistance of a stirring magnetic bar. Following this, 600 mg (2.116 mmol) of Compound 2 was introduced into the flask, accompanied by the addition of 5 drops of acetic acid, and the mixture was refluxed for 18 hours. After the reaction concluded, the reaction mixture was concentrated and poured into a beaker containing cold water, resulting in the formation of a white precipitate. This precipitate was subsequently filtered and subjected to multiple washes with water. Finally, the precipitate was dried to obtain the absolutely pure product as a white solid, yielding 486 mg (81%). Synthesis of polymer PNor-Flu was accomplished from Nor-Flu. It involves a ring-opening polymerization. Nor-Flu (0.0816 mmol, 1 eq.) was placed in a dried 10 mL polymerization vial under a complete nitrogen atmosphere and dissolved in 1 mL of dry DCM. Subsequently, a catalytic amount of Grubbs second-generation catalyst (0.01 eq.) was added by dissolving 200  $\mu$ L of dry DCM solution, and the reaction mixture was stirred at a specified temperature for 7 h under a nitrogen atmosphere. The polymerization reaction was then quenched using ethyl vinyl ether. The resulting reaction mixture was precipitated in diethyl ether to obtain a white solid random copolymer. Confirmation of polymerization was achieved through  $^1\text{H NMR}$  spectroscopy. Additionally, confirmation was obtained from Advanced Permeation Chromatography to get number average molecular weight and polydispersity index<sup>12-17</sup>.

## RESULTS AND DISCUSSION

### Photophysical studies of Nor-Flu

After successfully synthesizing Nor-Flu and PNor-Flu, it is the examination of its photophysical properties of the sensor application. It is anticipated that the sensor molecule would form a stable complex in the solution in the presence of copper ions, resulting in colourimetric responses. To achieve this, UV-Vis spectroscopic studies of Nor-Flu in the presence and absence of copper(II) ions was performed. Initially, optimization of the solvent

system by varying nonpolar to polar and protic to aprotic solvents was done.

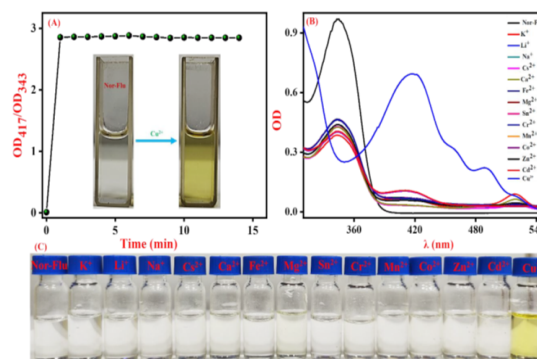


Fig. 1(A). Time-dependent study of the Nor-Flu (100  $\mu\text{M}$ ) in the presence of Copper (II) ions. (B) Selectivity study of the Nor-Flu (100  $\mu\text{M}$ ) in the presence of the different types of cations (100  $\mu\text{M}$ ) (C) Pictorial images of the Nor-Flu in the various metal ions in the naked eye

The present observations revealed that Nor-Flu exhibited an excellent response only in the case of DMSO. The photophysical studies of Nor-Flu were conducted in DMSO. It was observed that in the absence of copper ions, Nor-Flu showed an absorption peak at a wavelength of 343nm. However, in the presence of copper ions, Nor-Flu exhibited a new, red-shifted absorption peak at a wavelength of 417nm, accompanied by a change in the color of the solution from colorless to yellow. To determine the full response time of the monomer, a time-dependent study was carried out. This study revealed that the absorption maxima at 417nm reached saturation within one minute, indicating that the sensing of copper in the presence of Nor-Flu is instantaneous (Fig.1-A). To assess the selectivity properties of Nor-Flu, UV-Vis spectroscopic studies were performed in the presence of different types of metal ions. The results, shown in Fig.1-B and Fig.1-C, clearly indicated that Nor-Flu only responds in the presence of copper(II) ions, as evidenced by both UV-Vis spectroscopy and pictorial visualization. Having obtained positive results in the selectivity and time-dependent studies of Nor-Flu, it is quite essential to investigate its sensitive properties. UV-Vis spectroscopic titration of Nor-Flu with successive increases in the concentration of copper(II) ions from 0  $\mu\text{M}$  to 80  $\mu\text{M}$  was performed (Figure 2).

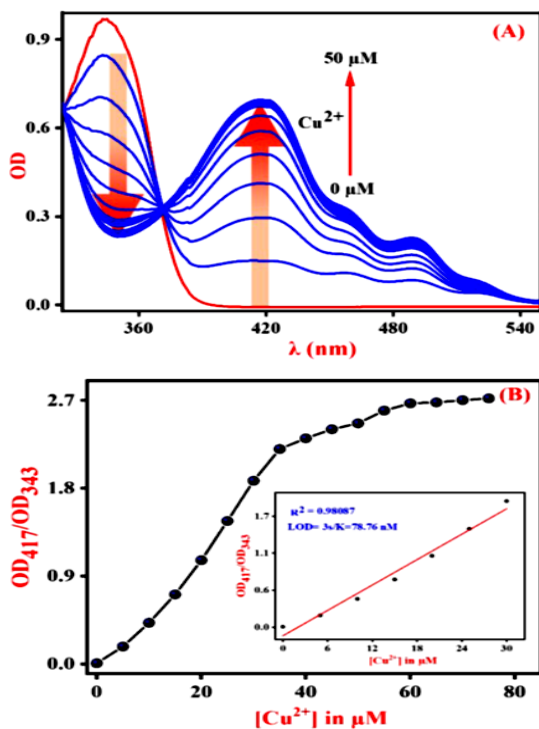


Fig. 2(A). UV-Vis spectroscopic titration of the Nor-Flu (100  $\mu\text{M}$ ) with increasing the concentration of the copper ions from 0  $\mu\text{M}$  to 80  $\mu\text{M}$ . (B) Titration curve of OD417/OD343 vs [Nor-Flu], Corresponding calibration curve of OD417/OD343 vs [Nor-Flu] in the lower concentration

A ratiometric titration curve was obtained, where the absorption maxima at 417nm increased and the absorption maxima at 343nm decreased with the addition of the copper(II) ions. It is observed that after adding 50  $\mu\text{M}$  of copper(II) ions, the absorption intensity at 417nm and 343nm became saturated. To determine the lower limit of detection of copper, the calibration curve has been drawn in the lower concentration region (0  $\mu\text{M}$  to 30  $\mu\text{M}$ ) and achieved an excellent linearity with  $R^2$  value of 0.98087. From the calibration curve, the LOD value of 78 nM was obtained, which is well below the limit provided by the WHO for environmental water. Based on the obtained results, it was found that Nor-Flu can detect copper(II) ions instantly with excellent selectivity and sensitivity, with an LOD of 78 nM.

### Determination of the binding constant and stoichiometry

The positive results in the case of selectivity, time-dependent study, and titration have motivated us to further investigate the photophysical properties of Nor-Flu, as shown in Fig. 3. It is hypothesized

that Nor-Flu forms a complex in the presence of copper(II) ions by creating a coordination bond with the nitrogen atom of the imine bond and the oxygen atom of the hydroxyl bond<sup>12-17</sup>. Additionally, ligand-to-metal charge transfer likely occurs during the formation of the complex, leading to the observed color change in the presence of copper(II) ions. The binding constant was determined from the UV-Vis titration to be approximately  $2.47 \times 10^5$ , using the Benesi-Hildebrand equation. Furthermore, employing Job's method, UV-Vis spectroscopy analysis was performed with increasing mole fraction of Nor-Flu and calculated a binding ratio of 1:2 for Nor-Flu and copper(II) ions.

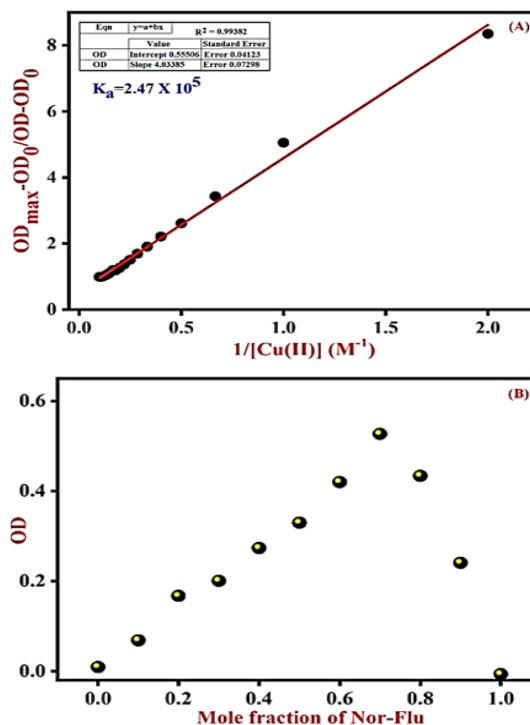


Fig. 3(A). Binding constant of Nor-Flu with copper, (B) Job's plot of Nor-Flu

### Photophysical studies of PNor-Flu

After achieving excellent results in the photophysical studies of the monomer (Nor-Flu), It proceeded to investigate the photophysical properties of the polymer (PNor-Flu). Although Nor-Flu demonstrates exceptional photophysical properties for the selective and sensitive detection of copper(II) ions, its practical application is limited. Due to the lack of amphiphilicity, the challenge lies in producing films, paper strips, and unique self-assembly properties. To overcome this issue,

synthesis was accomplished by ring-opening metathesis-based polynorbornenes for the selective and sensitive detection of copper(II) ions, as well as to study its host-guest self-assembly with copper(II) ions. Following the synthesis of the final polymer, the average molecular weight of PNor-Flu was determined using advanced polymer chromatography, which was found to be approximately 8000 Da with a PDI value of 1.10. To assess the photophysical properties of PNor-Flu, UV-Vis spectroscopic study was conducted in the presence and absence of copper(II) ions (Fig. 4). In the absence of copper(II) ions, PNorFlu exhibited an absorption peak at 350nm in DMSO. Upon addition of copper(II) ions to the PNor-Flu solution in DMSO, the peak at 350nm decreased, and a new red-shifted peak at 416nm emerged, accompanied by a change in the color of the solution from colorless to yellow.

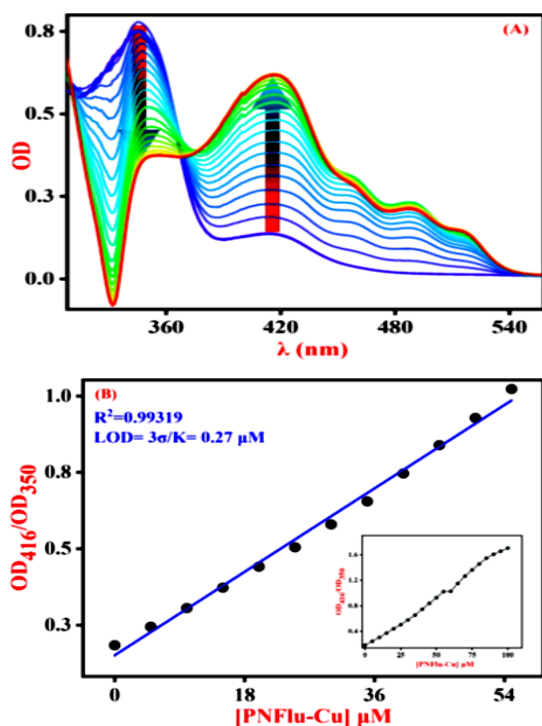


Fig. 4(A). UV-Vis titration of the PNor-Flu (100  $\mu\text{M}$ ) (100  $\mu\text{M}$ ) with increasing the concentration of the copper ions from 0  $\mu\text{M}$  to 100  $\mu\text{M}$ . (B) Calibration curve of  $\text{OD}_{416}/\text{OD}_{350}$  vs [PNor-Flu] in the lower concentration, corresponding titration curve of  $\text{OD}_{416}/\text{OD}_{350}$  vs [PNor-Flu]

Furthermore, a time-dependent study was performed to determine the time required for the complete sensing of copper(II) ions by PNor-Flu. The sensing of copper(II) ions by PNor-Flu is instantaneous, as the peak  $\text{OD}_{416}/\text{OD}_{350}$  reaches its

maximum within one minute after the addition of the copper(II) ions. Afterwards, the LOD was determined. For that purpose, the concentration-dependent UV-Vis titration of the PNor-Flu was obtained with the increase of the concentration of Copper(II) ions from 0  $\mu\text{M}$  to 100  $\mu\text{M}$ . It was observed that with an increase of the copper(II) ions concentration, the absorption maxima at 416nm increased and absorption maxima at 350nm decreased which suggests that it was ratiometric titration pattern with the isobestic point of 370nm. Also from the  $\text{OD}_{416}/\text{OD}_{350}$  vs concentration of the PNor-Flu at a lower concentration range, the calibration curve was plotted with an excellent  $R^2$  value of 0.99319 and from the  $3\sigma/K$  equation, the LOD of 0.27  $\mu\text{M}$  was obtained. So far the obtained result related to the PNor-Flu, it looks that like the Nor-Flu, PNor-Flu has a higher selectivity and the sensitivity of LOD value 0.27  $\mu\text{M}$  for the detection of the copper(II) ions instantaneously within one minute. The lower LOD value suggests that PNor-Flu can be utilized as a sensor for the detection of copper ions in environmental contaminants.

#### Morphological analysis of the PNor-Flu in the presence of copper(II) ions

Metal-based molecular self-assembly is another important aspect of this work. The results obtained in the sensing study of the Nor-Flu and PNor-Flu clearly show that a definite self-assembly pattern will be observed in the absence and the presence of the copper(II) ions. Along with that, a definite level of amphiphilicity is there in the polar solvent of PNor-Flu because of the presence of a large number of hydroxyl groups in the PNor-Flu. To check the morphological properties of the PNor-Flu, initially, the dynamic light scattering study of the PNor-Flu was done by increasing the concentration from 0.025 mg/mL to 0.05 mg/mL. It was observed that in between the concentration range from 0.03 mg/mL to 0.05 mg/mL the size of the PNor-Flu becomes fixed which is about to be 91nm. Also, from the same DLS study was repeated with the addition of the copper ions. In this case, the hydrodynamic diameter of 100nm with the concentration range of the polymer 0.035 mg/mL was obtained. Next work performed was checking the SEM images of the PNor-Flu in the presence and absence of the copper(II) ions. It was observed that in the absence of copper(II) ions, the PNor-Flu is showing rod-like self-assembly (Fig. 5, B, C). Whereas in the presence

of copper(II), it shows spherical-like self-assembly (Fig. 5, E, F). All the self-assembly properties were investigated in the THF and water 1:1 mixture. Each of the monomers contains three hydroxyl groups, they take part in higher-order hydrogen bonding in the polymeric form and form rod-shaped self-assembly. Whereas in the presence of the copper(II) ions, it is forming a coordination bond with the oxygen atom of the hydroxyl group next to the imine group which lifted the possibility of the hydrogen bonding. That's why in the presence of the copper(II) ions it forms spherical self-assembly.

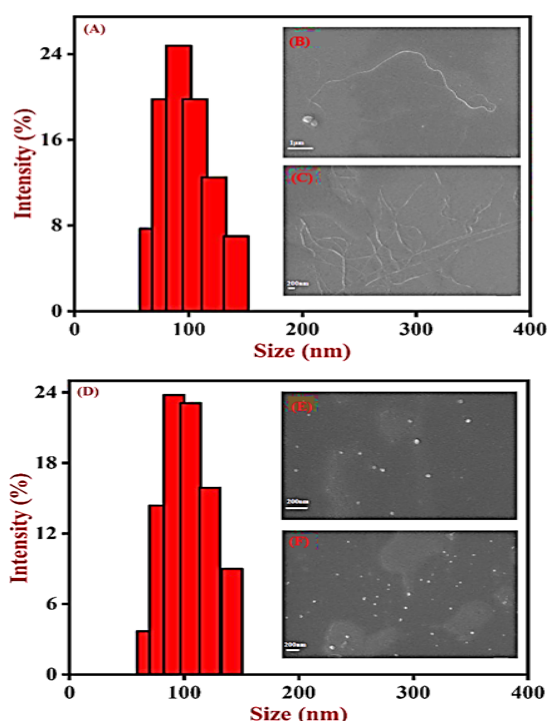


Fig. 5(A). DLS study of the PNor-Flu (0.03 mg/ml). (B, C) Corresponding SEM images of PNor-Flu (0.03 mg/ml). (D) DLS study of the PNor-Flu (0.03 mg/ml) in the presence of copper(II) ions (100  $\mu$ M) in water and THF 1:1 ratio. (E, F) Corresponding SEM images of PNor-Flu (0.03 mg/ml) in the presence of copper(II) ions (100  $\mu$ M) in water and THF 1:1 ratio

### Real sample analysis

It has been observed that copper(II) contamination often occurs due to the uncontrolled release of copper-based metal derivatives into the environment, which pollutes water bodies. To assess the ability of PNor-Flu to detect unknown amounts of copper(II) ions in environmental water, a real sample analysis was conducted. First, a calibration curve has been drawn using known concentrations of copper(II) ions in the presence of

PNor-Flu. Then, different unknown concentrations of copper(II) ions were introduced into pond water (India) and added a fixed concentration of PNor-Flu to each solution. Subsequently, UV-Vis spectroscopy was recorded and were compared the  $OD_{416}/OD_{350}$  with the calibration curve to determine the corresponding copper(II) ion concentrations. The present polymeric sensor PNor-Flu is capable of determining the unknown concentration of copper(II) in environmental contaminants with more than 98% accuracy (Table 1).

Table 1: Real sample analysis using PNor-Flu solution

| Sample          | Spiked, [Cu <sup>2+</sup> ] $\mu$ M | Obtained, [Cu <sup>2+</sup> ] $\mu$ M | % of accuracy |
|-----------------|-------------------------------------|---------------------------------------|---------------|
| Water in Pond 1 | 0                                   | 0                                     | 100           |
| Water in Pond 2 | 8                                   | 7.92 $\pm$ 0.104                      | 99.00         |
| Water in Pond 3 | 16                                  | 15.75 $\pm$ 0.235                     | 98.43         |
| Water in Pond 4 | 22                                  | 21.87 $\pm$ 0.355                     | 99.40         |
| Water in Pond 5 | 32                                  | 31.65 $\pm$ 0.025                     | 98.90         |

### CONCLUSION

Synthesis of the fluorescein-based polynorbornenes has been completed, PNor-Flu, for the selective and sensitive detection of copper(II) ions from environmental contaminants. Through concentration-dependent titration, it has been demonstrated that PNor-Flu exhibits very high sensitivity and selectivity for copper(II) ions, with a limit of detection (LOD) value of 0.27  $\mu$ M, which is lower than the limit permitted by the EPA. Additionally, It has been investigated the host-guest molecular self-assembly of PNor-Flu in the absence and presence of copper(II) ions. The present observations revealed that in the absence of copper(II) ions, PNor-Flu exhibits rod-like self-assembly, whereas in the presence of copper(II) ions, it forms spherical aggregates. Furthermore, present investigation based on real sample analysis indicates that PNor-Flu has an efficiency of over 98% in determining the copper(II) ion content in contaminated water.

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### Conflict of interests

There is no conflicts of interests in this work.

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