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Fluorescent macromolecular chemosensors for highly and selectively detecting of 2, 4, 6-trinitrophenol

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Abstract

Among nitroaromatic compounds with similar structures, 2,4,6-trinitrophenol (TNP) exhibits strong biological toxicity and explosion hazard. Therefore, detection of TNP is of great importance. In this work, two novel fluorescent macromolecular chemosensors P1 and P2 were prepared using borondipyrromethene (BODIPY) as the fluorophore. After the preparation of small BODIPY molecule M1, another small molecule M2 with two aldehyde groups was synthesized by two consecutive Vilsmeier–Haack reactions. Then, M2 reacts with trans-cyclohexane-1,4-diamine and 1,4-phenylenediamine respectively to obtain two macromolecules P1 and P2 via Schiff Base forming reaction. The results suggested that P1 and P2 could recognize TNP only while other aromatic/nitroaromatic compounds cannot cause significant fluorescence intensity response. When TNP exist, these fluorescent macromolecular chemosensors produce significant fluorescence quenching. At the same time, because the electron-rich Schiff base and the electron-deficient TNP have the structural basis of chemical interaction, these two macromolecular sensors also have excellent sensitivity to TNP, and the excellent recognition limit of detection reach as low as 0.017 μM. High sensitivity and selectivity have been applied to test TNP in lake water samples as well.

1. Introduction

It is well known that nitroaromatic compounds are not only flammable but also highly toxic [1]. 2,4,6-trinitrophenol (TNP) is one of the most active nitroaromatic compounds. Because of its explosive nature, TNP is widely used in fireworks, military explosives, etc [2] As a result of its toxicity; TNP could damage the eyes and skin [3], and even cause further damage to organs such as the liver and stomach [4]. Thereafter, it is a dangerous environmental pollutant to human health. Rapid, selective, and sensitive determination of TNP is increasingly of vital importance for the sake of safety and environmental protection [5].

Boosting the development of science and technology, there abound lots of methods to detect nitroaromatic compounds. Among them, the instrumental analysis method could be the most accurate and reliable one [6]. Classical instrumental methods for the determination of nitroaromatic compounds include gas chromatography (GC) [7], high performance liquid chromatography (HPLC) [8], capillary electrophoresis (CE) [9], UV−vis spectrophotometry [9], in situ infrared spectroscopy technique [10], X-ray imaging [11], molecular fluorescence spectrometry [12], electrochemical methods [13], etc. The downside, nevertheless, is that almost all of these methods are expensive and complex, requiring specialized laboratories to perform the appropriate analysis and testing, which is time-consuming and labor-intensive. What’s more, these expensive instruments often need professionals to carry out maintenance, labor costs are also a big expense. Therefore, the design and synthesis of efficient, sensitive, and fast fluorescent molecular sensors should be considered.

In recent years, the science and technology of fluorescent chemosensors have been proved to be a very promising method for TNP detection [6]. Compared with other common detection technologies, it has many advantages, including relatively high sensitivity and selectivity, low cost, portability, and so on [14, 15]. Several
studies have been done on the methods and applications of fluorescence analysis in previous studies, for example, Toal et al [16] used electron-deficient nitroaromatic compounds that had the characteristics of quenching luminescent polymers to detect nitroaromatic compounds. Ma et al [17] prepared fluorescent chemosensors specific to 2, 4, 6-trinitrophenol and 2, 4, 6-trinitrotoluene by electro polymerization. When the two nitrocompounds are present in the environment, they can be easily detected by this sensor. Stringer et al [18] have prepared an optical sensor for detecting 2, 4-dinitrotoluene using methyl methacrylate as a functional monomer. The limit of detection reaches 30.1 μM, and the response time can be as short as 1 min.

The above-mentioned studies have their advantages and characteristics. However, most of these fluorescent probe detection methods could be improved, such as to simplify the sophisticated synthetic route or to lower detection limit.

In our previous researches, we [19] have designed and synthesized two chemosensors by the Suzuki coupling reaction, and those sensors exhibit high selectivity and sensitivity to heavy metal ions such as Cd$^{2+}$ and Zn$^{2+}$ as well. In addition, we [20] introduced BODIPY into polyurethane, and the chemosensors have very good selectivity for Hg$^{2+}$ ion detection, the detection limit has reached 5 μM. These studies all use BODIPY as a substrate to synthesize a variety of different macromolecular chemosensors, which have specific recognition functions for different environmental pollutants, but the detection limit could be improved.

In this study, Boron-Dipyromethene (BODIPY) is employed as the fluorophore. Then, two aldehyde groups were generated from BODIPY by the Vilsmeier-Haack reaction in two consecutive steps as the starting materials of the synthesized macromolecule [21, 22]. Finally, two macromolecules with BODIPY units in the main chains were obtained by Schiff Base formation reaction with trans-1, 4-cyclohexanediamine and 1, 4-phenylenediamine respectively [23]. Compared to previous research [19], this study has better selectivity for nitroaromatics and lower detection limits, and the synthetic route is simple, the detection limit is more ideal, reaching as low as 0.038 μM and 0.017 μM respectively. Besides, they showed high selectivity and sensitivity to TNP, significant fluorescence quenching was observed when TNP was mixed with P1 or P2. Glass et al [24] have reported that, due to the quenching effect of the aldehyde group, the fluorescence of the probe will decrease, but after the reaction forms Schiff Base, the quenching effect of the aldehyde group will be inhibited, so that the fluorescence of the probe will increase significantly. In the real application of TNP detection in lake water samples, the macromolecular chemical sensors P1 and P2 also confirmed that the lake water was not contaminated by TNP.

2. Experimental section

2.1. Materials

4-Acetamidobenzaldehyde, 2,4-Dimethylpyrrolem, Trifluoroacetic Acid (TFA), Boron Trifluoride Etherate (BF$_3$·Et$_2$O), 2,3-Dichloro-5,6-Dicyano-1,4-Benzoquinone (DDQ), Triethylamine (Et$_3$N), Trans-1,4-Diaminocyclohexane, p-Phenylenediamine were all purchased from J&K China Chemical Ltd and used as received.

1,2-Dichloroethane (DCE), Tetrahydrofurran (THF), Phosphorus Oxychloride (POCl$_3$), Dichloromethane (DCM), N, N-Dimethylformamide (DMF), Glacial Acetic Acid and Ethanol were all purchased from Aladdin Chemical Co. Ltd. Deionized water was used through all the experiments.

2.2. Characterization

Fourier transform infrared spectra (FTIR, 4000 cm$^{-1}$–500 cm$^{-1}$) were operated on the Nicolet NEXUS 470 spectrometer. The fluorescence spectrum was carried out on Shimadzu F-4500 fluorescence spectrophotometer. $^1$H-NMR data was obtained by AVANCE III 600 MHz (Bruker). A great number of samples were studied on a UV–5900PC spectrophotometer (METASH) for UV–vis measurement. Gel Permeation Chromatography (GPC) was performed in a Polymer Laboratories PL–GPC 50 Plus integrated GPC system (Wyatt Technolo USA). The zeta-potential analyzer (Zetaplus, Brookhaven Instruments, USA) was used to test the zeta-potential versus pH values.

2.3. Synthesis

In this work, two small molecules M1 and M2 were synthesized first, and then they were used as precursors to prepare macromolecular chemosensors P1, P2. The precursor monomers M1 and M2 were designed and synthesized via Vilsmeier–Haack reaction and Schiff Base reaction [20, 21, 25]. The synthetic routes are described below and shown in scheme 1.
2.3.1. Synthesis of precursor monomer M1

The small fluorescent molecule M1 containing BODIPY moiety was synthesized by the following methods and procedures. At room temperature, 4-Acetamidobenzaldehyde (498.8 mg, 3.06 mmol) and 2,4-Dimethylpyrrole (654.4 mg, 6.88 mmol) were dissolved in 30 ml anhydrous mixed solvents with THF and DCM, compared with a single solvent, the mixture solvent can make the reactants more fully dissolved, and the final yield is higher. After 30 min, TFA (300 μl) was added and tin foil was used to avoid light treatment. The mixture was stirred and refluxed for 8 h under the nitrogen atmosphere. Then in the ice-bath condition, add DDQ (693.9 mg, 3.06 mmol) dissolved in 20 ml of DCM to the three-necked flask within 15 min, return to room temperature and continue stirring under reflux for 10 h. After that, Et3N (7.64 ml) was dissolved in a small amount of anhydrous DCM and slowly added to the reaction system over a period of about 15 min. After stirring and refluxing for 3 h, add BF3·Et2O (8.56 ml) to the flask under the ice bath conditions again. After maintaining the temperature for 30 min, return to room temperature and continue the reaction for 12 h. The solution was washed thrice with saturated sodium bicarbonate (NaHCO3) solution and DCM. The organic layers were merged and dried over anhydrous MgSO4 and then evaporated in a vacuum.

The crude products were purified by column chromatography (ethyl acetate: petroleum ether = 1:3) to obtain yellow M1 solids (701.8 mg, 1.84 mmol, yield 59.9%). MS of M1 calculated for C21H23BF2N3O [M] + 382.1908, found 382.1904. The mass spectrum can be seen in figure 1. 1H NMR analysis are indicating in the following (CHCl3, 400 MHz): δ (ppm): 1.00–2.50 (d, H-1, 2, 3, 4, 5), 3.50 (m, H-6), 5.25–5.50 (d, H-7), 6.00 (d, H-8), 7.00–8.00 (d, H-9, 10, 11, 12). Figure 2 reflected the 1H NMR spectra of M1. The FTIR analysis of M1 can be shown in figure 1.

2.3.2. Synthesis of precursor monomer M2

The synthesis of M2 using M1 as starting material is carried out by two consecutive Vilsmeier–Hack reactions [26]. Under the nitrogen protection and ice bath condition, add POCI3 (3.10 ml) to DMF (3.10 ml) dropwise over about 10 min until a gelatinous Vilsmeier salt appears. After stirring for 20 min, it was allowed to warm to room temperature while stirring was continued. M1 (350 mg, 0.92 mmol) was dissolved in DCE (20 ml) and added to the reaction system, followed by raising the temperature to 60 °C and stirring for 8 h. After cooling to room temperature, the reaction mixture was poured into saturated sodium bicarbonate (NaHCO3) solution and DCM. The organic layers were merged and dried over anhydrous MgSO4, and then evaporated in a vacuum.

The crude products were separated and the organic layers were merged. The aqueous layer was washed repeatedly with DCE and dried over anhydrous MgSO4, and it was evaporated under vacuum. Follow the above steps and repeat the Vilsmeier-Haack reaction again to get the M2 crude products. The pure M2 products were obtained by column chromatography (ethyl acetate: petroleum ether = 1: 1) as red
solids (60 mg, 0.14 mmol, yield 30%). MS of M2 calculated for C_{23}H_{23}BF_2N_3O_3 [M]^+ 438.18, found 438.94. The mass spectrum can be seen in figure 1. \(^1\)H NMR analysis is indicating in the following (CDCl\(_3\), 400 MHz): \(\delta\) (ppm): 1.00–2.50 (d, H-1, 2, 3, 4, 5), 3.50 (m, H-6), 7.00–8.00 (d, H-7, 8, 9, 10), 9.75–10.25 (s, H-11, 12). Figure 2 reflected the \(^1\)H NMR spectra of M2. The FTIR analysis of M2 can be seen in figure 1.

2.3.3. Synthesis of macromolecular chemosensors P1 and P2
Two macromolecular fluorescent chemosensors, P1 and P2, were synthesized by Schiff Base reaction [23, 27, 28]. Dissolve Trans-1, 4-Diaminocyclohexane (15 mg, 0.13 mmol) in absolute alcohol, add it to a three-necked flask, heat to 60 °C under N\(_2\) protection; then dissolve M2 (61 mg, 0.14 mmol) with absolute alcohol and dropwise add it to the reaction system. 15 \(\mu\)L of glacial acetic acid were further added, the temperature was raised to 80 °C, and the mixture was refluxed for 6 h. As the reaction proceeds, the product will gradually precipitate on the wall of the glass container. After the reaction was finished, the product is scraped and washed with ethanol for centrifugation 4–5 times, and then dried in a vacuum drying box for 24 h. The pure P1 product was obtained as blue-black solids (55 mg, yield 90%).

The route of P2 which was obtained by the Schiff Base reaction is similar to that of P1. 1, 4-phenylene diamine (12 mg, 0.11 mmol) was dissolved in absolute alcohol, stirred and heated to 55 °C under the protection of N\(_2\). M2 (51 mg, 0.12 mmol) was then dissolved in anhydrous ethanol and added into the reaction system. Then add 10 \(\mu\)L glacial acetic acids and immediately raise the temperature to 80 °C. After 6 h of reflux, the product will gradually subside on the wall of the glass container. After the reaction, the product was removed and centrifuged with ethanol for 4–5 times, and then dried in a vacuum drying oven for 24 h. The pure P2 product was obtained as deep-blue solids (48 mg, yield 95%). The FTIR analysis of P1 and P2 can be shown in figure 1.

3. Results and discussion

The structures and properties of M1, M2, P1 and P2 were studied. The results are exhibited and discussed as following paragraphs.

3.1. Structural characterization of small molecule and macromolecular chemosensors
The \(^1\)H NMR spectra of the two precursor small molecules M1 and M2 are shown in figure 2. In figure 2 (M1), the peak at 1.0–2.5 ppm is the chemical shift of multiple methyl hydrogens (H1, H2, H3, H4, H5), the peak at
3.5 ppm is the chemical shift of pyrrole cyclic hydrogen (H6), the two peaks at 5.3 ppm and 6.0 ppm are the two hydrogens (H7, H8) directly connected to the carbon-carbon double bond on the pyrrole ring. After performing two continuous Vilsmeier–Hack reactions on M1, the 1H NMR spectrum of M2 is shown in figure 2 (M2). The most significant difference is that a new chemical shift peak appears at around 10 ppm, and this is the characteristic peak of aldehyde hydrogen (H11, H12). The results indicate that two small molecules M1 and M2 were obtained.

Figure 2. The 1H NMR spectra of M1, M2.
The results of FTIR exhibited that two macromolecular chemosensors were successfully synthesized. The FTIR curve of polymers and its corresponding information can be observed from figure 1. The characteristic absorption peak at 3440 cm\(^{-1}\) should be caused by the stretching vibration of the nitrogen-hydrogen bond. The two small absorption peaks at 2920 cm\(^{-1}\) and 2850 cm\(^{-1}\) may be caused by the stretching vibration of carbon-oxygen double bonds of aldehyde groups at both ends of the macromolecule. It is worth mentioning that with the reaction from M2 to P1 and P2, it can be seen that the strength of peaks at 2920 cm\(^{-1}\) and 2850 cm\(^{-1}\) decreases significantly, which proves that the aldehyde groups successfully participate in the Schiff Base reaction. The absorption peak at 1630 cm\(^{-1}\) may be caused by the carbon-oxygen double bond stretching vibration in the acetyl group or the carbon-nitrogen double bond stretching vibration on the Schiff Base imine. The difference between the two macromolecules is that P2 has three distinct moderate-intensity absorption peaks appeared near 1520 cm\(^{-1}\), which are characteristic absorptions of the benzene ring skeleton vibration, and it also matches the fact that the P2 has multiple benzene rings.

In addition, the molecular weight and molecular weight distribution of P1 and P2 were determined by GPC. As can be seen from table 1, the molecular weights of the two macromolecules P1 and P2 are both over 5000 g mol\(^{-1}\), indicating that they reached the level of macromolecules, and of near mono-dispersity.

### 3.2. Detection of nitroaromatic/aromatic compounds

#### 3.2.1. UV–vis absorption analysis

The specific recognition of nitroaromatic compounds by P1 and P2 was first investigated by UV–visible spectroscopy. The testing results are shown in figure 3.

To study the effect of pH on chemosensors P1 and P2, Britton–Robinson buffer solution was used. P1 and P2 were dissolved in DMF buffer solution, as can be seen from figures 3(a), (b), chemosensors did not show significant change in the pH range from 11.98 to 1.81, indicating that they were available over a wide pH range.

To study the effect of adding different nitroaromatic compounds on absorbance, figure 3(c) shows that after TNP is added to P1, the absorbance suddenly increases, and the wavelength corresponding to the maximum absorption peak is at 372 nm. The wavelength and absorbance of other nitroaromatic compounds did not change obviously after they were added. Figure 3(d) also shows a similar change, with the addition of TNP, the wavelength decreases and the absorbance increases significantly. The photos inserted in figures 3(c) and (d) are also included, which are shown under natural light. The changes of color after adding TNP are very obvious, while the remaining nitroaromatic compounds have not changed significantly, those significant changes could be seen with unaided eyes in figure 5. In order to better study the selectivity of P1 and P2, in addition to some common nitroaromatic compounds, four aromatic compounds have been added as other compounds. They are benzoic acid (BA), aniline (AN), methylbenzene (MB) and phenol (P), the structural formula of other compounds could be seen in scheme 2.

#### 3.2.2. Fluorescence spectroscopy analysis

The ability of macromolecular chemosensors P1 and P2 to specifically recognize nitroaromatic compounds was studied by fluorescence spectroscopy. Figure 3 has shown the results. Figure 3(e) shows the fluorescence spectra at an excitation wavelength of 340 nm, and P1 shows a fluorescence emission peak at 463 nm. After adding 10 equivalents of other nitroaromatic compounds, TNP caused obvious fluorescence quenching, and as a comparison, the pure P1 sample itself and other various nitroaromatic compounds did not change much in fluorescence intensity. The photo inserted in figure 3(e) show that under UV light, this significant change in fluorescence quenching can be seen with unaided eyes. The same results are also presented in figure 3(f). This result shows that the two sensors P1 and P2 have good performance for TNP, the recognition ability can be used to distinguish them from other nitroaromatic compounds.

The binding constants of P1, P2 and their sensitivity to different concentrations of TNP were further studied by fluorescence titration. The results have been shown in figure 4. It can be seen from the figure 4(a) that as the concentration of TNP increases from 0 to 10 equivalents (0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 μM), the fluorescence intensity of the chemosensor P1 gradually decreases. Similarly, as shown in figure 4(b), the fluorescence intensity of the P2 sensor also decreases as the concentration of TNP increases. The fluorescence photos of other nitroaromatic compounds can be seen with naked eyes in figure 5. The trend is consistent with the actual measurement data. According to the limit of detection (LOD) calculation formula and the linear slope of P1 and

| Sample | M_n (g mol\(^{-1}\)) | M_w (g mol\(^{-1}\)) | P1 |
|--------|----------------------|----------------------|----|
| P1    | 5800                 | 6700                 | 1.15 |
| P2    | 7000                 | 7200                 | 1.03 |
In figures 4(c), (d) to obtain the standard slope, the detection limits of P1 and P2 sensors can be calculated. The calculation formula for LOD is:

\[
LOD = \frac{3\alpha}{K}
\]

In the equation (1), \(\alpha\) is the standard deviation of the sensor when measuring a blank sample; \(K\) is the absolute value of the slope of the fitting line. By calculating the detection limit, we can obtain that the detection limits of P1 and P2 for TNP are 0.038 \(\mu\)M and 0.017 \(\mu\)M, respectively. It can be seen that P2 is more sensitive to TNP.
As shown in Table 2, through the comparison of LOD of various polymer materials for TNP, it can be determined that this study has a certain application value for TNP in the detection environment.

The fluorescence quantum yield of the probes before and after sensing was also tested, it is listed in Table 3.

The fluorescence quantum yield experiment was conducted with Rhodamine B ($\phi = 0.97$) in ethanol solution as the standard solution and calculated using the following equation:

![Scheme 2. Structural formula of nitroaromatic/aromatic compounds.](image)

![Figure 4. P1 (a) and P2 (b) fluorescence changes (DMF-buffer solution) with unequal amount of TNP from 0 to 10 equivalent for P1 and P2. $\lambda_{ex}(P1) = 340$ nm, $\lambda_{ex}(P2) = 360$ nm. Detection limits of TNP for P1 (c) and P2 (d).](image)
In the equation (2), $x$ is the solution to be tested, $s$ is the standard solution, $\phi$ refers to the quantum yield, $F$ represents the integrated area under the emission curve, $A$ stands for the absorption intensity at the excitation wavelength and $n$ exhibits index of refraction of the solution.

To better understand the detection performance of the sensor on nitroaromatic compounds and the difference in appearance under different concentration gradients, physical pictures were taken under natural light and ultraviolet light respectively, as shown in figures 5 and 6.

In addition, chemosensors P1 and P2 are also applied in real samples. Water samples were taken at two different locations in the university’s lake, and then P1 and P2 were added to them to observe the changes in fluorescence intensity, and compare the fluorescence intensity when P1 and P2 were combined with TNP. It can be seen from figure 7 that the lake water was not polluted by TNP.
To better comprehend the binding characteristics, the binding rate of macromolecular chemosensors were well studied by job plot analysis. The total concentration of the sensor and TNP was maintained at 10 μM, which caused a certain change in the concentration ratio of the sensor and TNP. The difference between the maximum fluorescence intensity between the theoretical value $I_0$ and the actual value $I$ is used as the ordinate, and the value of the ion concentration compared to the total concentration is used as the abscissa. As shown in figure 8, it can be seen that the coordination ratio of these two chemosensors to TNPs is 1:2 (chemosensor: TNP). For P1 and P2, it can be speculated that each chemosensor has two $\text{–C}=\text{–N}$ bond, which could coordinate with TNPs. In the mechanism part, the change of infrared wavelength confirms this hypothesis.

Figure 7. Fluorescence changes of chemosensors with lake water and TNP (10 μM).

Figure 8. Job’s plots of P1 (a) and P2 (b), Stern-Volmer plot of P1 (c) and P2 (d).
The Stern-Volmer equation can be applied to the static quenching system with stoichiometric ratio of 1: n, and can be used to calculate the stability constant of the complex formed by the metal ion probe. The quenching constant of these two chemosensors can be calculated by Stern-Volmer equation:

\[
\Delta \text{lg } F = \text{lg } F_0 - \text{lg } F = \text{lg } K_a + n \text{lg } [Q]
\] (3)

In the formula (3), \(F_0\) and \(F\) are the fluorescence intensity of the system in the absence or in the presence of quenching agent, respectively. \(K_a\) is the Stern-Volmer quenching constant, \([Q]\) is the concentration of quenching agent, and \(n\) is the number of binding sites between two molecules.

Taking \(\frac{\text{lg } F_0 - \text{lg } F}{\text{lg } Q}\) as the ordinate and \(\text{lg } [Q]\) as the abscissa, a linear regression could be obtained in figure 8. By calculation, the quenching constant \((K_a)\) of P1 and P2 can be determined as \(7.4 \times 10^3\) and \(7.9 \times 10^3\), respectively.

The interference effects of other nitroaromatic compounds on the detection of TNP in P1 and P2 were studied. It can be seen from figure 9(a) that when other nitroaromatic compounds are added, there is no significant interference with TNP. In addition, as shown in figure 9(c), compared with other nitroaromatic compounds, TNP is the only nitroaromatic compound that can be selectively recognized by P1, and the fluorescence intensity is almost doubled, this effect has a greater change than that of P2. Figures 9(b), (d) shows the ability of TNP to be specifically recognized by P2. Other interfering nitroaromatic compounds did not significantly interfere with the detection of TNP by P2, and the fluorescence intensity of P2 increased by 120%. Taken together, these two macromolecular sensors can be used in most environments.

3.2.3. Zeta-potential analysis

To demonstrate the presence of valence electrons in the macromolecular Schiff Base, P2 was tested with zeta potential study as a representative. The zeta-potential versus pH curves of the P2 probe is shown in figure 10. The isoelectric points (IEP) of macromolecular chemosensor P2 was at around pH 4.2, and zeta-potential was up to +2 mV was obtained at pH 3.78. Therefore, this observation provides good evidence that valence electrons are located on the surface of the Schiff Base and affect the zeta potential of macromolecules. At low pH, Schiff Base is protonated and therefore cationic, which results in a positive zeta potential.
3.2.4. Detection mechanism
To better understand the sensor’s binding mechanism to TNP, P1 and P1 with TNP were selected for FTIR experiments. Figure 11 (Left) shows the FTIR spectra. After adding TNP, obvious changes can be seen easily. Multiple intermediate-intensity peaks have been added around 1300 cm\(^{-1}\)–1500 cm\(^{-1}\). This is a peak generated by the typical skeletal vibration of the benzene ring, and the two peaks at 700 cm\(^{-1}\) and 900 cm\(^{-1}\) also prove that the bonded benzene ring is a meta-trisubstituted structure. Also, the peak shape and peak intensity of the small peak near 1500 cm\(^{-1}\) in P1 infrared have changed significantly, indicating that –C=\(\equiv N\)– has undergone significant changes after the addition of TNP [33]. All these wavenumbers and peak shape changes indicate that the –C=\(\equiv N\)– bond in the macromolecular sensor may be the binding site. Apart from that, as a negatively-charged Schiff Base, it is easy to combine with a positively-charged TNP [34]. This charge relationship structurally ensures that the macromolecular chemosensors can interact with TNP. According to the above inference, the possible mechanism of P1 and P2 binding to TNP can be seen from figure 11 (Right).

In addition, the macromolecules P1 and P2 belong to chemosensor rather than chemodosimeter. Because P1 and P2 bind to nitroaromatic compounds by coordination, this is the same as chemosensor. Chemodosimeter, on the other hand, requires chemical reactions with specific electrolytes to perform its functions, these reactions result in a significant chemical transformation including both the breaking and formation of several covalent bonds. This process generally irreversible, reflects accumulative response related directly to the concentration of the analyte, and shows high selectivity and sensitivity. Clearly P1 and P2 do not fall into this category.
4. Conclusions

In this work, two BODIPY unit containing macromolecular chemosensors P1 and P2 with fluorescence functions were successfully synthesized. They are both selective and sensitive to TNP. The quenching effect of the aldehyde group will weaken the fluorescence effect of the probe, but after the reaction is made into Schiff Base, the quenching effect of the aldehyde group will in turn be inhibited, thus significantly enhancing the fluorescence. Through the study of the detection limit of the sensor and the interference ions, it is found that the detection effect of P1 is better, while the sensitivity of P2 is even better. This article may provide a new idea for easily synthesizing high-efficiency TNP sensors.

Conflicts of interest

The authors declare no competing financial interest.

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