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UPPER-RIM NITRO AND LOWER-RIM METHOXY FUNCTIONALIZED CALIX[4]ARENE BASED COLORIMETRIC SENSOR FOR DETECTION OF 2,4,6-TRINITROPHENOL

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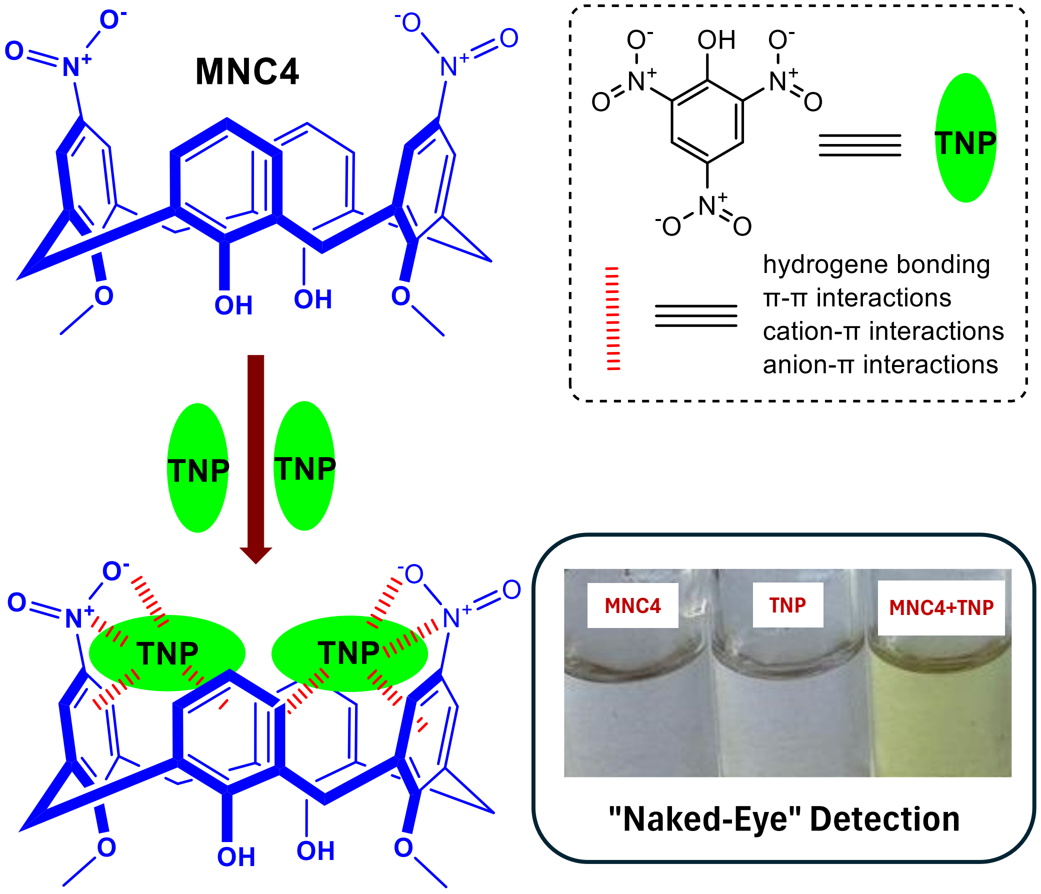
Highlights

- Calixarene-based colorimetric sensor (**MNC4**) was developed for 2,4,6-trinitrophenol (TNP).
- **MNC4** was a naked-eye sensor for TNP.
- **MNC4** had a limit of detection at nanomolar level (520 nM).
- The stoichiometric ratio of **MNC4**: TNP complex was 1:2.

Graphical Abstract



Mechanism of complexation of **MNC4** with TNP and naked-eye sensor image

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ABSTRACT: The development of effective sensors capable of detecting 2,4,6-trinitrophenol (TNP), or picric acid, at extremely low levels is a very interesting field of study for prevention of environmental contamination and terrorist threats. Therefore, in this study, a colorimetric sensor (**MNC4**) based on calix[4]arene containing a chromophore group was prepared for the detection of TNP. The photophysical interaction of **MNC4** with target nitroaromatic compounds (NACs) was evaluated using UV-Vis. spectroscopy. The initial **MNC4** solution was colorless, but a distinct color change was observed in the case of TNP, indicating a stronger binding affinity with **MNC4**. Spectral investigations also confirmed the relatively strong complexation between **MNC4** and TNP. The limit of detection (LOD) value for TNP was found to be 520 nM, indicating that **MNC4** can detect TNP down to the nanomolar level, which is significantly lower than the permissible level (2.2 μM). The stoichiometric ratio of the complex formed between **MNC4** and TNP was determined to be 1:2. The developed sensor enables the colorimetric detection of TNP with the naked eye without the need for any instrumentation, highlighting its potential for real-world applications.

Keywords: *Trinitrophenol, Calixarene, Colorimetric Sensor, Nitroaromatic Compounds, Explossive*

1. INTRODUCTION

The prevalence of anti-terrorism and security issues, especially in populated areas, has prompted the advancement of techniques for the trace detection of hazardous explosive substances. Detecting explosives with high sensitivity and selectivity has therefore become a critical security issue. Nitroaromatic compounds (NACs) represent an important class of frequently utilized explosive materials [1]. In recent years, the sensitive and selective detection of NACs has garnered significant attention due to their threat to humanity and national security. These explosives are also environmental contaminants and are recognized as toxic to living organisms [2]. NACs tend to decompose through exothermic processes and produce toxic gases and vapors [3]. Structurally, NACs are electron-deficient π-systems, and the increase of nitro groups on the benzene ring causes the electron deficiency to increase further [1].

2,4,6-Trinitrophenol (TNP), or picric acid, is a potent organic acid among NACs, and because it is more explosive than TNT and other similar nitroaromatic explosives, it was widely used in the military up until World War I [2]. Because of its widespread use, TNP poses serious health risks, including respiratory system damage and skin irritation, whereas its partially reduced form, picramic acid, is ten times more mutagenic than TNP [4, 5]. TNP is extensively utilized in the production of rocket fuel, as well as in the colored glass and paint industries [6, 7]. It is also an important component in the rocket fuel, matchbox, electric battery, and fireworks industries [8]. TNP is a water-soluble explosive released into the environment because of anthropogenic activities in industries, and it is found as a pollutant in wastewater, aquatic systems soil and air [9-11]. TNP in humans can increase skin sensitivity, weaken the immune system, cause methemoglobinemia, headaches, liver damage, and anemia. It can also harm respiratory organs due to bioamplification and bioaccumulation [12]. TNP is a well-known environmental pollutant that degrades slowly in biosystems and can cause serious health problems such as cancer, abnormal liver

***Corresponding Author:** Begüm TABAKCI, btabakci@selcuk.edu.tr functions, sycosis, and damage to kidneys and respiratory organs [13]. Therefore, the creation of effective sensors that can identify TNP at extremely low levels to stop environmental contamination and terrorist threats is an extremely interesting area of study [14, 15]. At this point, the development of a highly selective "naked eye" probe is a highly desirable goal [16].

Many detection techniques, including ion mobility spectroscopy (IMS), high-pressure liquid chromatography, surface-enhanced Raman spectroscopy, and electrochemical techniques, have been used to identify explosives. [17-20]. Nonetheless, existing techniques have certain limitations in practical application, including reduced stability, low selectivity, rapid response, lack of portability, challenging on-site operation, complex equipment requirements, and easy sample preparation [16]. Optical approaches present numerous advantages over conventional detection strategies, including cost-effectiveness, portability, high sensitivity, and selectivity, making them particularly appealing and promising solutions. In fact, fluorescence and colorimetric sensors have emerged as a promising analysis technique in recent years, with a variety of new materials being designed and synthesized in this area [21]. For example, functionalized small organic molecules, metal or nonmetal nanoparticles, metal organic frameworks (MOFs), etc. [22-27]. It is still very difficult to develop appropriate soluble and effective organic chemosensor with high selectivity for TNP, even though different π-electron-rich organic polymers and metal-organic architectures have been used to detect the presence of electron-rich nitro-aromatics [28]. As a result, many recently developed optical sensors for explosive detection focus primarily on absorbance (colorimetric) and fluorescence responses [29, 30].

Supramolecular chemistry, centered on host-guest interactions and self-organization, initially utilized preorganization for the development of customized molecular receptors that facilitate molecular recognition of metal ions, anions, and chiral molecular substrates [31-33]. In particular, the recognition of neutral guests has received a lot of attention because of their biological and environmental significance [34]. To develop a selective and sensitive chemosensor, a significant amount of research has been conducted to understand how the properties of the host-guest complex are altered when a specific analyte is introduced [35, 36]. Nevertheless, there are relatively few examples of color change-based detection methods in classical chemical analysis, despite their convenience as a visual detection method [34].

Calixarene, a third-generation supramolecular compound, has been widely utilized in molecular recognition, materials science, supramolecular self-assembly, catalysis, and various other applications due to its unique structure and properties [37, 38]. Calixarenes can be readily modified at the upper or lower rim to form complementary interaction sites with the analyte [39-41]. In addition, the cavity of the calix platform is also used for capturing guest molecules [42]. Calixarenes are appealing host compounds with large uncharged rings and a naturally hollow cavity-like structure. Such macrocyclic compounds have conformational preferences due to their ease of chemical modification, which makes them suitable for complexation with various analytes. The cup-shaped cavity of calixarenes, combined with their functionalized backbone, can provide selectivity and additional binding sites for analytes [43].

Moreover, fluorophores that are reported for TNP detection are characterized by fluorescence quenching. The disadvantage of these sensors is that fluorescence quenching is challenged by the flexibility of the excited state of the species, the strong interaction between the excited state and the lattice, and background fluorescence fluctuations [6]. This is the reason why sensors that operate through fluorescence at the turn-on state are becoming increasingly popular, despite their scarcity in literature. A considerable number of Fluorescence-based molecular probes for the detection of NACs have been reported in literature. However, there are limited studies focusing on the selective recognition of TNP [44]. In addition, there are only a few supramolecular systems based on calixarene that have been reported to selectively recognize TNP, and all these receptors rely on fluorescence quenching mechanism for detection. Given these limitations and shortcomings, developing a calix[4]arene-based colorimetric sensor for the simple, rapid, and selective detection of TNP has become an important goal. Therefore, in this study, in connection with our ongoing search for sensors for biologically and environmentally important guest species [37, 45-49], we present a colorimetric receptor (**MNC4**) that recognizes TNP specifically *via* hydrogen bonding or π-π interactions. In this context, a calix[4]arene derivative (**MNC4**) bearing two methoxy groups in the lower rim and two nitro groups in the upper rim was synthesized and characterized, and its ability to selectively recognize TNP was investigated using UV-Vis. spectroscopy. Selectivity was assessed by comparing data on five other NAC guest molecular species.

2. MATERIAL AND METHODS

The structural characterization of the synthesized molecules was carried out with Varian brand 400 MHz NMR spectrometer. Spectrum 100 FTIR spectrometer model from PerkinElmer was used for FTIR spectra analysis. During the syntheses, reactions were monitored using Merck brand Kieselgel 60 F_{254} thin layer chromatography. UV-Vis. studies were performed with PG instruments brand T80 UV-Vis. spectrophotometer model. Melting point values were determined with a Stuart-SMP3 melting point apparatus. All aqueous solutions were prepared with distilled water obtained using a Millipore Milli-Q Plus water purifier. All chemicals and reagents used during the study were of analytical quality and were purchased from Merck, Sigma Aldrich, Alfa Aesar, and ISOLAB. All spectroscopic analyses were repeated at least three times to ensure a high level of precision and accuracy in the results obtained. For the synthesis of the calix[4]arene-based receptor (**MNC4**) targeted in this study, the synthesis scheme given in Figure 1 was followed according to the methods in the literature [37, 43, 50].

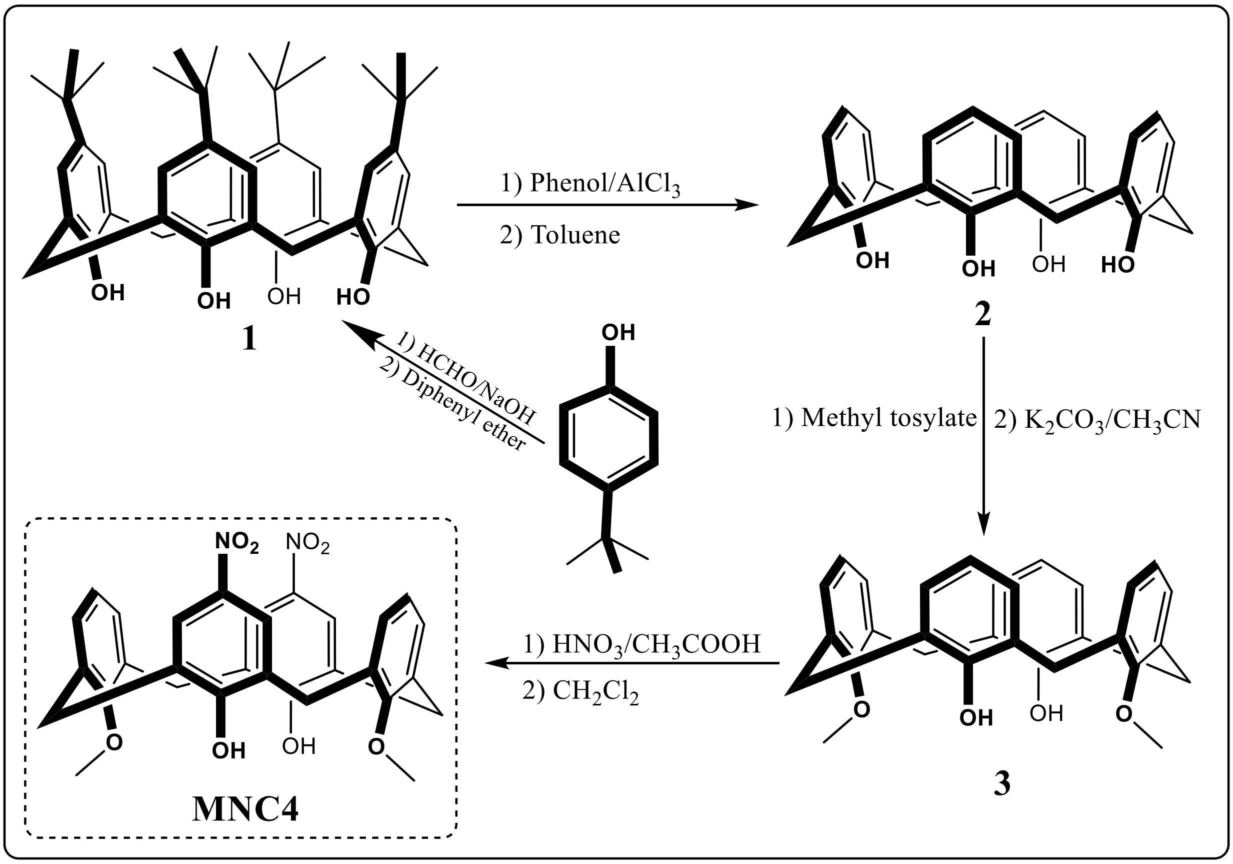
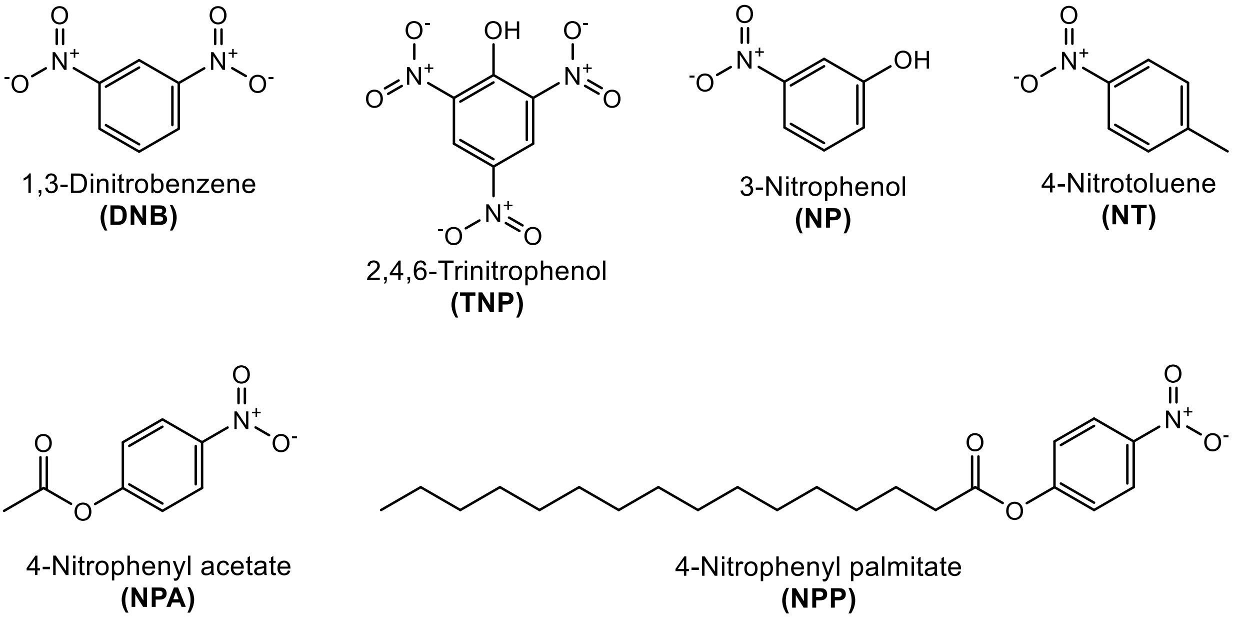


Figure 1. Synthesis scheme of **MNC4**

The interaction between **MNC4** containing chromophore group and NACs (Figure 2) in the solution phase was investigated using UV-Vis. spectroscopy. Stock solutions of **MNC4** and NACs were prepared at a concentration of 1.0×10^{-2} M in DMSO and acetonitrile, respectively. Before the UV-Vis. studies, it was examined the colorimetric changes that can be observed with the naked eye under visible light. For this purpose, 1.0 equivalent of NAC was added to 3.0 mL (99:1 v:v) CH_3CN-H_2O solution (99:1) containing 1.0×10^{-5} **MNC4** and color changes were monitored. UV-Vis. analysis of the respective complexes was then performed. Thus, changes in the absorption spectrum of **MNC4** when NAC was added were noted and analyzed to find out which species formed complexes and how much they formed.



1,3-Dinitrobenzene **(DNB)**

2,4,6-Trinitrophenol **(TNP)**

3-Nitrophenol **(NP)**

4-Nitrotoluene **(NT)**

4-Nitrophenyl acetate **(NPA)**

4-Nitrophenyl palmitate **(NPP)**

Figure 2. NACs used in the study and their molecular structures

3. RESULTS AND DISCUSSION

The main aim of this study was to synthesize a calix[4]arene derivative (**MNC4**) bearing a chromophore group and to investigate its sensing properties against NACs. In this context, firstly, the synthetic route shown in Figure 1 was followed for the synthesis of the nitro group bearing calixarene derivative exhibiting colorimetric properties, and the structures of the produced compounds were confirmed by FTIR and ^{1}H-NMR spectroscopy. The photophysical interaction of **MNC4** with target NACs was then evaluated using UV-Vis. spectroscopy.

3.1. Synthesis of MNC4 sensor

In the synthesis studies, the starting compound *p-tert*-butylcalix[4]arene (**1**) was synthesized by condensation reaction of *p-tert*-butyl phenol with formaldehyde in the presence of NaOH. Compound **2** was then synthesized by a dealkylation reaction of compound **1** with phenol in toluene in the presence of $AlCl_3$ according to the procedure in the literature [51]. In the next step, compound **3**, a derivative of *p-tert*-butylcalix[4]arene bearing two methoxy groups from the lower rim, was synthesized according to the previously reported procedure [50]. For this purpose, compound **2** was refluxed with methyl tosylate in acetonitrile in the presence of potassium carbonate for 24 hours. Finally, **MNC4**, which contains two methoxy groups in the lower rim and two nitro groups in the upper-rim of calix[4]arene, the main target compound of the study, was synthesized by adopting the procedure in the literature [50]. For this purpose, the nitration reaction of compound **3** was carried out in acetic acid and dichloromethane by interacting with nitric acid at room temperature for 12 hours. The structure of all compounds obtained after purification was confirmed by several analytical techniques including melting point, FTIR, and ^{1}H-NMR spectroscopy. In this context, in the ^{1}H-NMR spectrum of **MNC4** given in Figure 3, the formation of a new signal corresponding to 4H at 8.26 ppm belonging to the aromatic rings to which NO_2 groups are attached and the signals of aromatic para hydrogens at 6.83 ppm corresponding to 2H confirmed the structure. In addition, the observation of a vibration band of NO_2 groups at 1526 cm^{-1} in the FTIR spectrum of **MNC4** supported the characterization.

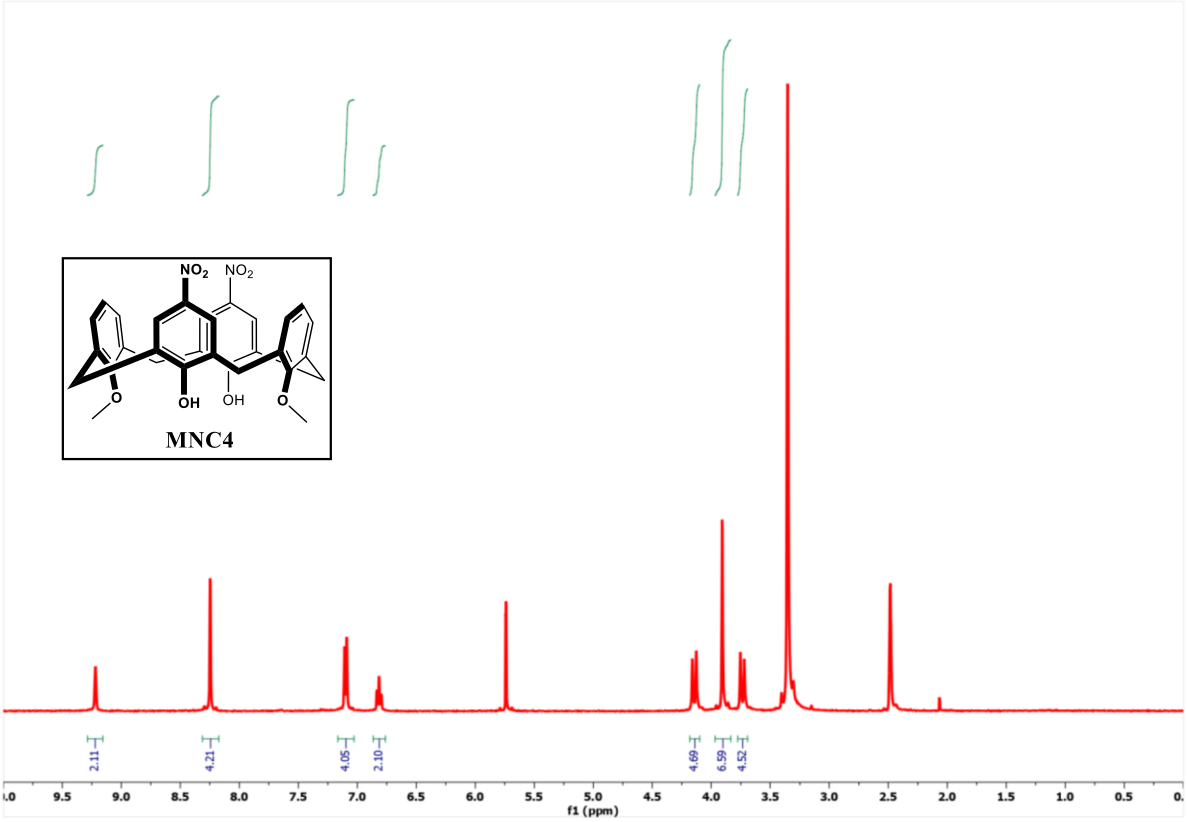


Figure 3. ^{1}H-NMR spectrum of **MNC4**

3.2. UV-Vis. Absorption Studies

Preliminary studies were conducted with the naked eye to determine the colorimetric response of **MNC4** to NACs. In this context, up to 10.0 equivalents of NAC were added to 1.0×10^{-5} M CH_3CN-H_2O solutions (99:1) of **MNC4**. In addition, 1.0 g of soil sample was added to each sample to see the compatibility with real environments, as NACs are likely to be highly present in soils. The initial **MNC4** solution was colorless, which is favorable for detection applications given the more distinctive color change that occurs upon exposure to NAC. Visual inspection with the naked eye under visible light showed that TNP exhibited a distinct color change in contrast to other NACs (Figure 4a). In other words, no significant color change was observed when other NACs were added, while the color of the solution turned yellow in the case of TNP. This result indicated that TNP has a much stronger binding affinity with **MNC4**. It is known from the literature that H-bonding and π-π interactions between **MNC4** and TNP structures are effective in this binding [44]. In the next step, UV-Vis. absorption spectra of all prepared samples were taken. It is clearly seen from the spectra given in Figure 4b that TNP exhibits an absorption that confirms its strong interaction with **MNC4**. In the corresponding UV-Vis. spectra (Fig. 4b), the formation of a new absorption band at about 350 nm is in good agreement with this color change.

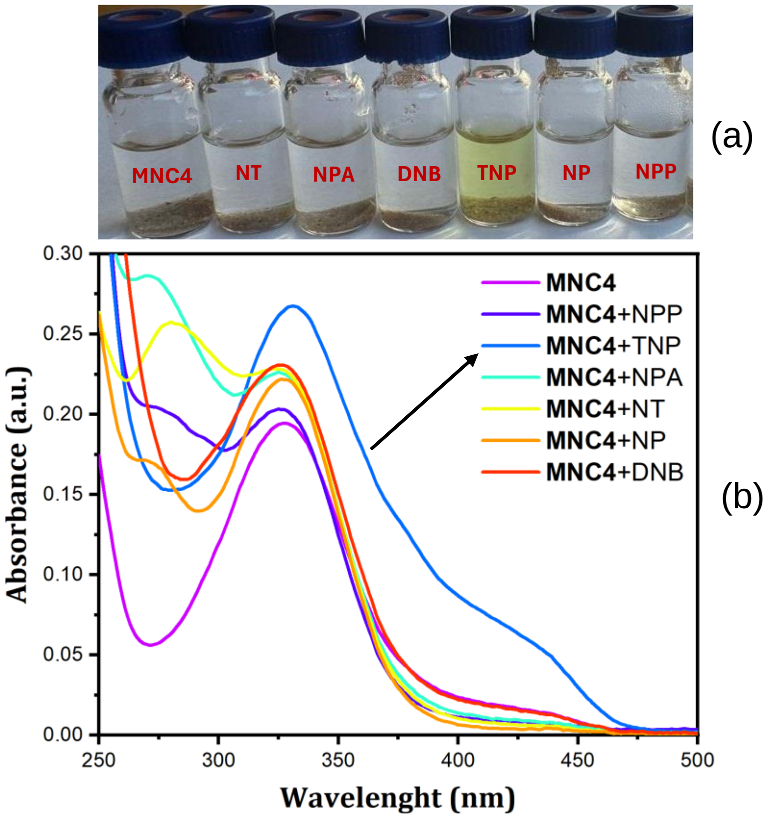
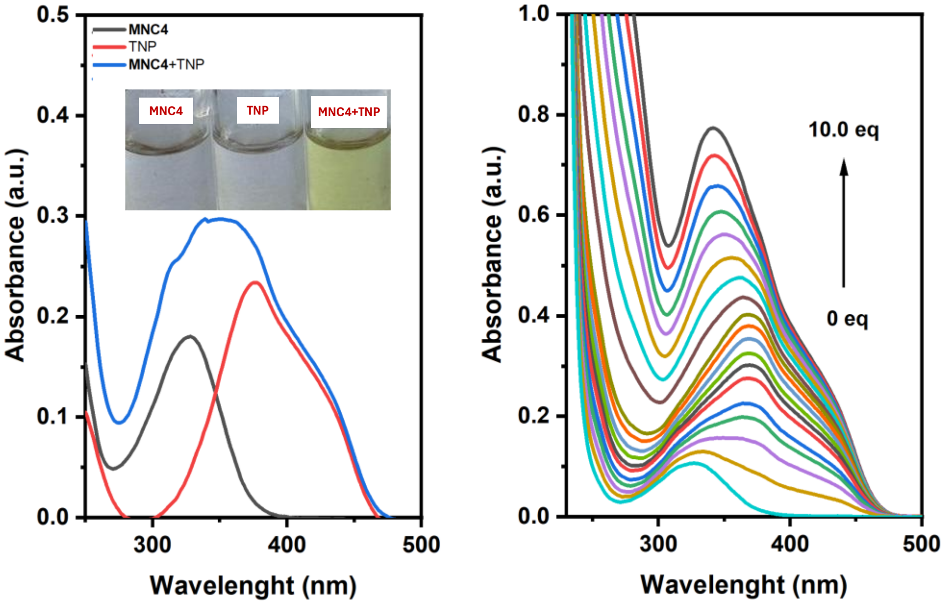


Figure 4. Color changes (a) and absorption spectra (b) of **MNC4** ($1.0x10^{-5}$ M) after addition of 10.0 equivalents of various NACs in CH_3CN-H_2O (99:1, v/v).



(a) (b)

Figure 5. UV-Vis. spectra of (a) the interaction of **MNC4** with TNP (inset image is the corresponding photographs of the solutions), (b) **MNC4** upon addition of 0-10.0 eq. TNP (([**MNC4**] = $1.0x10^{-5}$ M in CH_3CN-H_2O (99:1, v/v))

TNP had the strongest visual response and absorption when it interacted with **MNC4**. Therefore, further research was done on the complexation of **MNC4** with TNP. To confirm the complex formation, solutions of **MNC4** and TNP were first prepared in CH_3CN-H_2O (99:1, v/v) and UV-Vis. spectra were taken separately. Then, 10.0 equivalent TNP were added to the solution containing only **MNC4**, and the UV-Vis. spectrum of the solution was taken. As can be seen in Figure 5a, three broad absorption spectra with different maximum wavelengths of 329 nm, 376 nm, and 350 nm were observed for **MNC4**, TNP, and **MNC4**-TNP complex, respectively. Thereupon, titration studies were carried out up to 10.0 equivalent TNP to determine the photophysical parameters of 1.0×10^{-5} M **MNC4** characterizing the complex formed, and the results are given in Figure 5b.

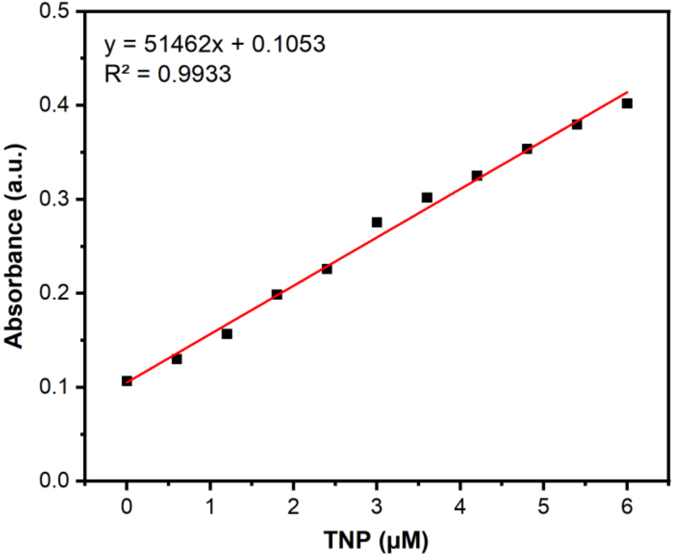


Figure 6. Linear absorbance plot at 350 nm versus 0-6.0 µM TNP added on **MNC4** ([**MNC4**] = $1.0\text{x}10^{-5}$ M in CH_3CN-H_2O (99:1, v/v)).

From the data obtained from the titration of **MNC4** with TNP, a linear regression of absorption versus TNP concentration was performed as shown in Figure 6. Based on the data from the straight-line part (0-6.0 µM) of this graph, the limit of detection (LOD) value was found to be 520 nM using the formula LOD = $3\sigma/m$, where σ is the mean difference between 10 blank samples and m is the slope of the linear regression. This result reveals that **MNC4** can detect TNP down to the nanomolar level, a value significantly lower than the permissible level (2.2 µM) of TNP [52]. As a result, with increased absorption, the sensor will have extremely low detection limits and thus can be used in real-world scenarios.

The Job's plot given in Figure 7a was used to determine the stoichiometric ratio of the complex formed between **MNC4** and TNP [37]. Considering that the maximum absorbance occurred close to the 0.33 mole fraction, it was concluded that the complexation occurred in a 1:2 ratio. In addition, to support the stoichiometry of **MNC4** complexation with TNP, the binding phenomena under the same conditions were also studied using the Benesi-Hildebrand equation (Equation 1) [37].

$$\frac{1}{A-A_0} = \frac{1}{\{K(A_{max}-A)[TNP]\}} + \frac{1}{(A_{max}-A)} \quad (1)$$

Here, A_0 is the initial absorbance, A is the absorbance after TNP addition, A_{max} is the maximum absorbance value obtained, and K is the binding constant (1/M). Accordingly, the K value for complexation was calculated as $5.6\text{x}10^3\,M^{-1}$ from the graph drawn with the Benesi-Hildebrand equation (Figure 8b) using the titration data. In addition, the fact that the graph is far from linearity indicates that complexation does not occur at a 1:1 ratio.

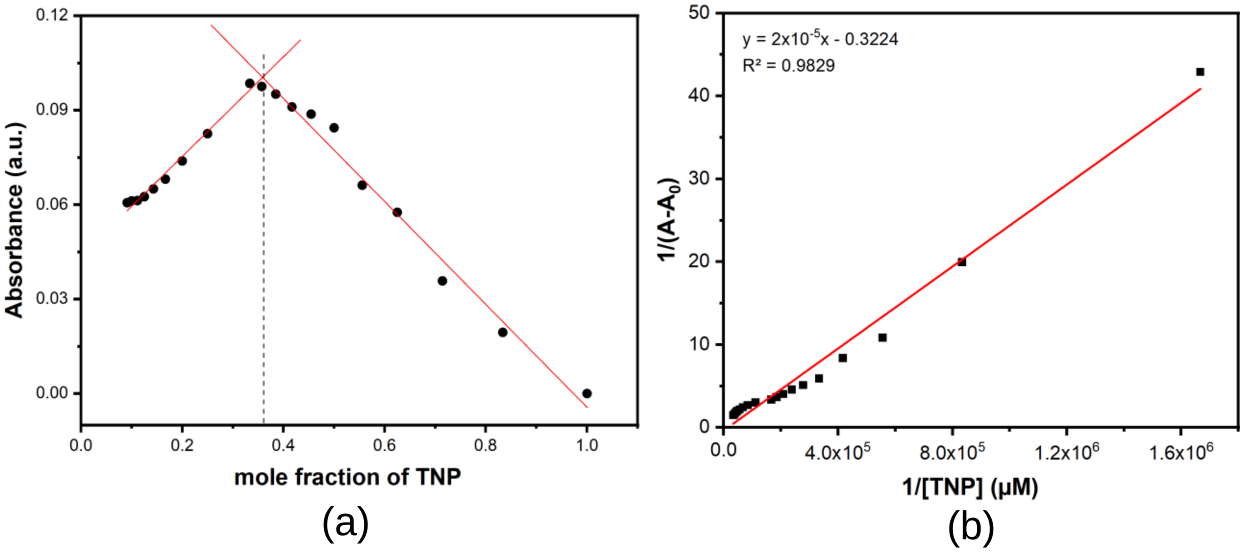


Figure 7. (a) Job's and (b) Benesi-Hildebrand plot for complexation of sensor **MNC4** with TNP in $CH_3CN–H_2O$ (99:1, v/v)

Although not directly, the developed sensor has been compared with some other TNP sensors, considering certain characteristics such as the detection limit, the material used, and the detection method. From Table 1, most of the sensors reported for TNP detection are less sensitive compared to the sensors developed in this study, with the limitations and disadvantages mentioned in the introduction. It can also be added that the current sensor enables colorimetric detection of TNP with the naked eye without the need for any instrumentation. The better LOD compared to the UV-Vis. spectrometric based sensor in the table can be interpreted to the calixarene skeleton of **MNC4**.

Table 1. Comparison of the current work with previously reported works on TNP detection

Method	Material used	Detection limits	Reference
Flow injection electrochemical	Copper electrode	6.0 μM	[53]
Electrochemical	Reduced graphene oxide	0.54 μM	[54]
Fluorescence	Triphenylamine based compound 1	≈1.75 μM	[55]
Luminescence	ZnO quantum dots	2.86 μM	[56]
UV-Vis.	L probe, it contains N-(rhodamine-B)lactam-ethylenediamine and 4-(9H-carbazol-9-yl)benzoyl group	820 nM	[16]
UV-Vis.	Calixarene based	520 nM	Current work

4. CONCLUSIONS

The aim of this study was to synthesize a calix[4]arene derivative (**MNC4**) bearing a chromophore group and to investigate its sensing properties against nitroaromatic compounds (NACs). For this purpose, a calixarene derivative bearing a nitro group on the upper rim and a methoxy group on the lower rim was synthesized and its structure was confirmed by FTIR and ^{1}H-NMR spectroscopy. The photophysical interaction of **MNC4** with target NACs was evaluated using UV-Vis. spectroscopy. Preliminary studies were carried out to determine the colorimetric response of **MNC4** to NACs, which can be observed with the naked eye. The colorless **MNC4** solution showed a color change from colorless to yellow when interacting with TNP, thus the clearest visual response was observed. UV-Vis. absorption spectra of NACs also confirmed this selectivity. The LOD of the sensor **MNC4** was calculated to be significantly lower (520 nM) than the permissible level of TNP (2.2 μM). The stoichiometric ratio of the complex formed between **MNC4** and TNP was determined as 1:2 and the binding constant value for complexation was calculated as $5.6 \times 10^3\ M^{-1}$. The developed sensor has demonstrated its potential for real-world applications by enabling colorimetric detection of TNP with the naked eye without the need for any instrumentation.

DECLARATION OF ETHICAL STANDARDS

The authors declare that all ethical guidelines including authorship, citation, data reporting, and publishing original research are followed.

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Clever Ng'andu: Investigation, Validation, Writing – original draft preparation.

Begum Tabakci: Conceptualization, Methodology, Supervision, Funding acquisition, Writing – Review & Editing.

Mustafa Tabakci: Methodology, Investigation, Visualization, Writing – Review & Editing.

DECLARATION COMPETING INTEREST

The authors declare that there is no conflict of interest.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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