

# A Review on Recognition of Explosives using Calixarene Framework

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**Abstract:** In terms of social security and support, quick, ultra-sensitive, and ultra-selective detection of explosives is urgently needed around the world. This review is ardent to calixarene a recent selective and sensitive explosive sensor. The structural binding properties of the Calix system and macromolecules can be modified by various structural mode changes and interactions, and multiple possibilities of functionalization of the calixarene make these versatile molecules in the phenomena of specific recognition. This study reflects on the use of fluorescence-based chemosensors for explosive detection that has been mentioned in the literature. From this review, it is implied that calixarene excellently complexes with high selectivity explosives and attraction associated with other simple ion receptor applications using different ions.

**Keywords:** calixarene; analyte; explosive; chemosensor; host-guest interaction.

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## 1. Introduction

For the rapid, sensitive, ultra-selective detection of explosives, ‘Quick and reliable Calixarene based Chemosensor’ plays a significant role in the military venture, national defense, forensic investigations, and environmental and human well-being [1-6]. The explosive is made up of a combination of reducing and oxidizing agents that, when activated, will undergo a strongly exothermic reaction, resulting in gaseous materials that can kill people [7]. Nitroaromatic compounds are common explosives, but they are also considered environmental pollutants in the areas where they're made and handled [5]. Trinitro aromatic concentrations in groundwater and soil surrounding an exploded explosively can exceed 500 parts per billion (ppb) and 1000–5000 parts per million (ppm), respectively [8]. When TNT is digested or inhaled, it can cause skin irritation, kidney disease, and irregular liver functions [5]. TNT also has a detrimental impact on male fertility and is now considered a significant human carcinogen [9]. As a result, the US Environmental Protection Agency (EPA) has imposed a TNT cap in drinking water of 2 ppb[5,9]. Face irritation, yellow-tinged hair and skin, body fatigue, and muscle discomfort are among the health risks associated with exposure to such explosives [10-15].

## 2. Recognition methods

Trained coonhounds, metal detectors, and ion mobility spectrometry (IMS) are now widely appropriate technologies for explosive detection. However, coonhound training is costly, and dogs quickly wear out from constant sensing, making it unsuitable for widespread and long-term tracking [16]. IMS is a widely used explosive detection device in air stations, with specificity down to nanograms or picograms for typical explosives. However, this technique lacks sufficient sensitivity for various explosives, such as PETN and RDX, limiting its overall effectiveness. Furthermore, IMS is inappropriate for real-time field detection because it requires complex protocols, time-consuming calibration, and poor portability and high cost [17].

A range of instrumental techniques is currently available for the purpose of explosives detection; these include GC- MS, Raman spectroscopy, X-ray imaging, nuclear quadrupole resonance, thermal and fast neutron analysis, ion mobility spectrometry, and various spectroscopic methods. Metal detectors are an indirect method that is very effective for detecting landmines and weapons contained in metals. However, they are not susceptible to the chemical fingerprint properties of explosives. They, therefore, cannot be used for transit site screening [17].

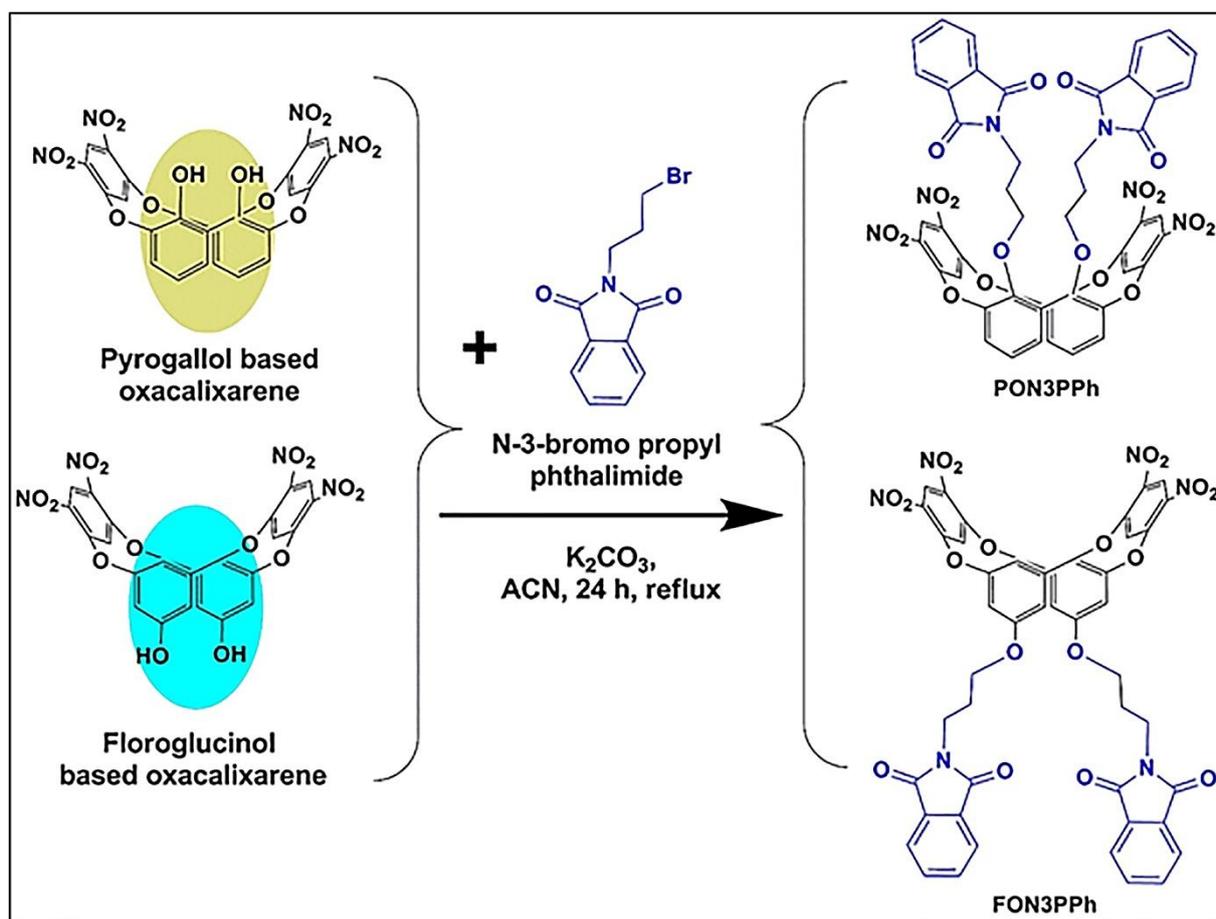
Optical approaches, which have many advantages over other common detection strategies, such as low cost, portability, high sensitivity, and selectivity, are especially appealing and promising solutions. As a result, the main target of many newly designed optical sensors for explosive detection is absorbance (colorimetric) and fluorescence responses [3]. As compared to absorbance-based techniques, fluorescence-based detection is usually one to three orders of magnitude more effective and has broader linear ranges. Furthermore, a fluorescence method's source and detector may be conveniently combined into a portable device for explosives detection in the field. As a result, the fluorescence-based approach holds much promise for rapid, sensitive, and selective explosive detection. These include photo-induced electron transfer (PET), fluorescence (Förster) resonance energy transfer (FRET), excimer/exciplex formation or extinction, and photo-induced charge transfer (PCT).

Importantly, the most recent advancements in this area have been structured into a concise outline that intends to rationally outline the various techniques and enhancements in the use of fluorescent material for explosive detection.

Calixarenes are attractive host compounds possessing large uncharged rings and an inherent hollow cavity-like architecture [18,19]. Such macrocyclic compounds have conformational preferences due to the ease with which they can be chemically modified, which is favorable for the complexation of different analytes. The cup-shaped cavity of calixarenes, along with the functionalized backbone (organic moieties), will provide selectiveness and extra binding sites for analytes [18,20,21]. Recent work has been summarized with a focus on the research in the recent 5 years.

Recently, Panchal *et al.* designed new structural motifs based on oxacalix[4]arene appended N-(3-bromopropyl) phthalimide moiety, FON3PPh, and PON3PPh, and examined their fluorogenic activities against nitroaromatic explosives. FON3PPh has a linear concentration range of 5 M to 4.5 mM for 4-NT, with a detection limit of 2.4 M, and a linear concentration range of 0.5 M to 5 mM for 2,6-DNT, with a detection limit of 0.1 M [22]. FON3PPh and PON3PPh have binding abilities for 4-NT and 2,6-DNT of  $1.15 \times 10^4 \text{ M}^{-1}$  and

$3.02 \times 10^4 \text{ M}^{-1}$ , respectively [23,24]. They studied anti-proliferative action using a cell cytotoxic assay [25-28].

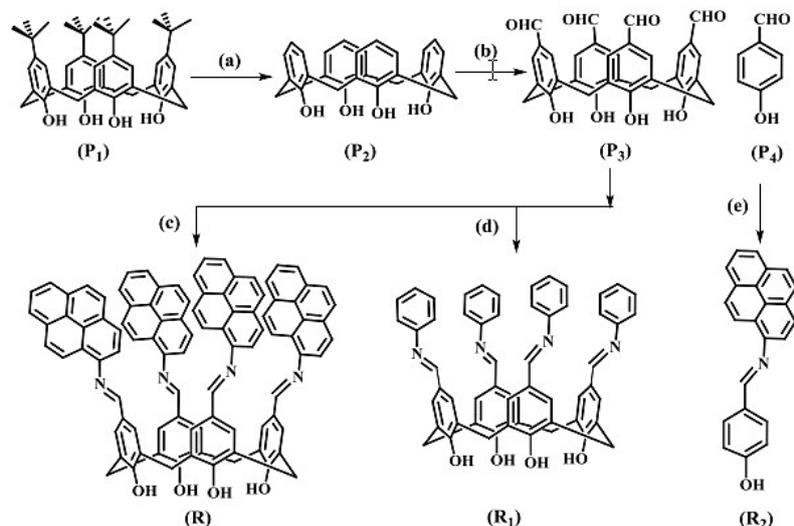


**Figure 1.** Synthetic route for the preparation of PON3PPh and FON3PPh.

Rao *et al.* have developed a 1,3-Di-naphthalimide Conjugate of Calix[4]arene as a Sensitive and Selective Sensor for Trinitrophenol by conjugating an upper rim of calixarene with a tetrapyrenyl moiety. Two other control molecules tetraphenylhydroxy benzene (R1) and p-pyrenyl-hydroxy benzene (R2), were synthesized to best understand the function of the calix[4]arene platform and pyrenyl moieties in R that lacks the calix[4]arene platform. The R exhibits high sensitivity to TNP in tetrahydrofuran (THF) over eleven other nitroaromatic compounds (NACs) studied by exhibiting significant fluorescence enhancement, indicating that it is selective to TNP over the other NACs.[29]. On the other hand, control molecules R1 and R2 suggest that a calixarene platform and a tetrapyrenyl moiety in the receptor system are needed for TNP selective sensing. Fluorescence titration and isothermal titration calorimetry have been used to study TNP binding to R. The numerical calculations revealed the existence of TNP complexation by R, with the data revealing TNP entrapment by two adjacent pyrene moieties through stacking interaction. The mobility of the pyrene moieties present in R should be limited due to such host-guest complexation. The  $^1\text{H}$  NMR spectral analysis indicates that TNP binding decreases the stability of the pyrenyl moieties of R, which serves as additional evidence for the complexation. TNP sensing by R has been demonstrated in THF solution, on the surface of a silica gel, and on the surface of cellulose paper, with the lowest detection threshold (LODs) of 1.5, 3.5, and 6.5 M, respectively.

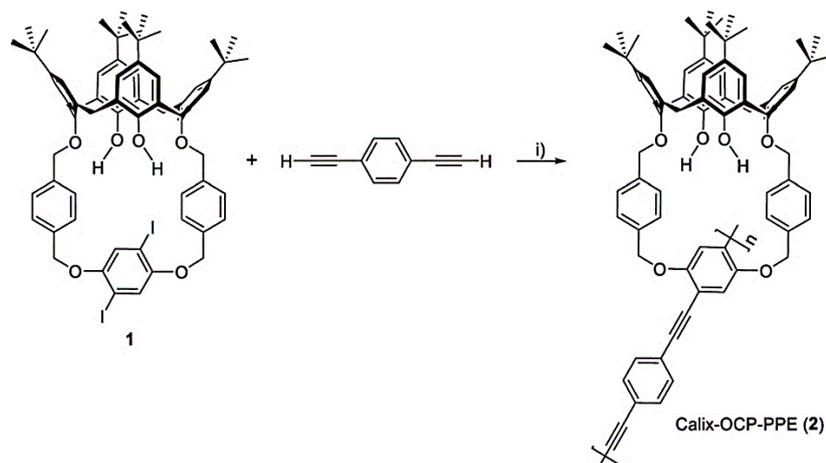
LOD of 2.1 mole was observed in a solid mixture of R and TNP. Because supramolecular aggregation of R is expected to depend on the guest species, the corresponding

details were investigated using microscopy techniques such as scanning electron microscopy, atomic force microscopy, transmission electron microscopy, and significant changes in R aggregation upon interaction with TNP were observed. The observed fluorescence enhancement is due to this aggregation. As a result, the tetrapyrrenyl calix[4]arene conjugate (R) serves as a sensitive and reliable platform for detecting TNP in a mixture of nitroaromatic compounds (NACs) with different fluorescence intensities [30-35].



**Figure 2.** (a) Anhydrous AlCl<sub>3</sub>, phenol, toluene, stirring at room temperature (RT) for 24 h; (b) hexamethylenetetramine, trifluoroacetic acid, reflux 24 h and then dil. HCl, stirring at RT for 6 h; (c) 1-amino pyrene, benzoic acid (catalytic amount), toluene, heated at 110 °C for 5 days; (d) aniline, benzoic acid (catalytic amount), toluene, heated at 110 °C for 3 days; (e) 1-amino pyrene, benzoic acid (catalytic amount), toluene, heated at 110°C for 24 h.

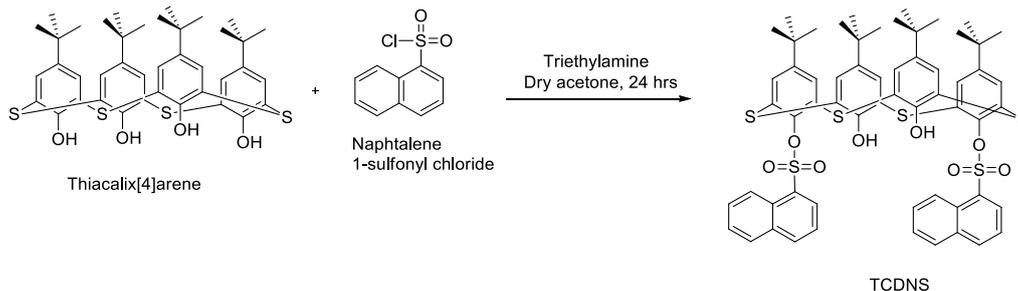
Prata *et al.* developed a new conjugated polymer (Calix-OCP-PPE (2)) with a main chain phenylene ethynylene interface tethered to Macromolecular receptors based on oxacyclophane-calixarene units and examined its potential uses as a solid-state fluorescence sensing device. Polymer 2 was structurally characterized, and its optical properties in solution and casted films were determined. The ability of polymer 2 to detect two sets of electron acceptor aromatics (NACs and NAs) in the vapor process was explored for demonstration purposes. Thin films of 2 proved to be excellent sensing platforms for sensitive and selective identification of nitroaromatics (2,4-DNT and TNT) and isomeric nitro anilines. The explanations for polymer 2's separate sensing capabilities against these analytes were explored. [36].



**Figure 3.** Synthesis of Calix- OCP-PPE (2): (i) PdCl<sub>2</sub> (PPh<sub>3</sub>)<sub>2</sub> and CuI (catalytic amounts), NEt<sub>3</sub>/toluene, 35 °C, 48h.

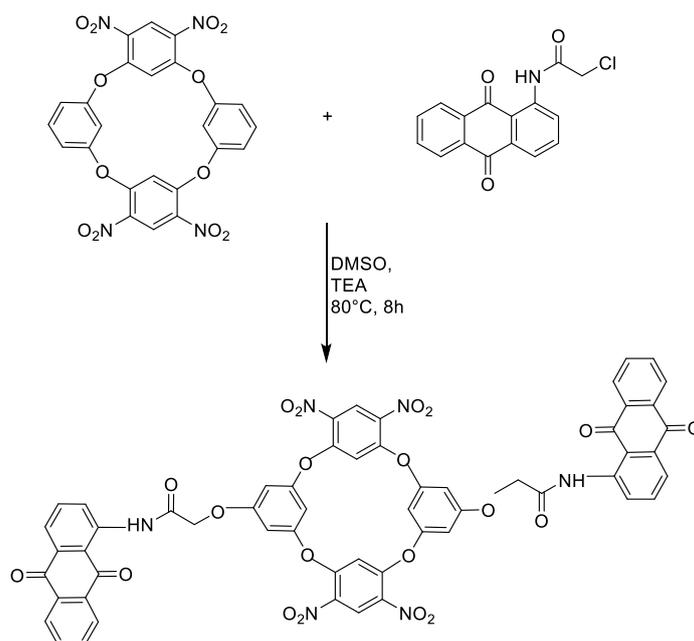
Modi *et al.* invented a global fluorescent thiacalix[4]arene dinaphthalene sulfonate (TCDNS) by combining thiacalix[4]arene with naphthalene sulfonyl chloride in 2018. <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and ESI-MS spectrometric measurements were used to classify the TCDNS.

The spectrofluorimetric technique was used to investigate the selectivity of fluoroionophore for 4-nitrotoluene (4-NT) and 2,3-dinitrotoluene (2,3-DNT) among various nitroaromatic compounds (NACs). TCDNS emission is deeply quenched by 4-NT and 2,3-DNT. ESI-MS and <sup>1</sup>H NMR analysis support the complexation of TCDNS with 4-NT and 2,3-DNT. The identification of 4-NT and 2,3-DNT in a water sample was made using a normal addition process. Molecular docking and dynamics simulation techniques have been used to assist the forming of complexes between TCDNS 4-NT and TCDNS 2,3-DNT [1,37-39].



**Figure 4.** Synthesis of thiacalix[4]arene bis-naphthalene sulfonate.

Jain *et al.* identified DAQTNOC(5,17-di(N-(9,10-dioxo-9,10-dihydroanthracen-1-yl)acetamide) tetranitrooxacalix[4]arene), a fluorescent oxacalix[4]arene-based receptor for the basic detection of N-methyl-p-nitro aniline (MNA). DAQTNOC, among a variety of grenades, exhibits selective behavior for MNA in the absorption and emission spectra. Furthermore, using docking, molecular dynamics simulations, and time-dependent density functional theory, statistical insights were gained to study the inclusion complex's stability and spectroscopic analysis (TD-DFT). Van der Waals forces and hydrophobic interactions with MNA selectively stabilized DAQTNOC, resulting in a low-energy complex. These results are particularly intriguing because MNA is a well-known insensitive munition that has been observed for the first time using the Oxacalixarenes framework [40-42].



**Figure 5.** Synthetic route for the preparation of anthraquinone-appended Oxacalix[4]arene.

Zhan *et al.* presented tetraphenylethylene (TPE)-based Oxacalixarenes with traditional aggregation-induced emission (AIE) properties, and these Oxacalixarenes demonstrated good detection capability for nitroaromatic explosives [43]. In addition, as a base labile alkylating agent, N-(3-bromopropyl) phthalimide (N3PPH) has been condensed with various organic ligands. [44,45]. To achieve a low detection range, sensors based on fluorescence methods are recommended [46,47].

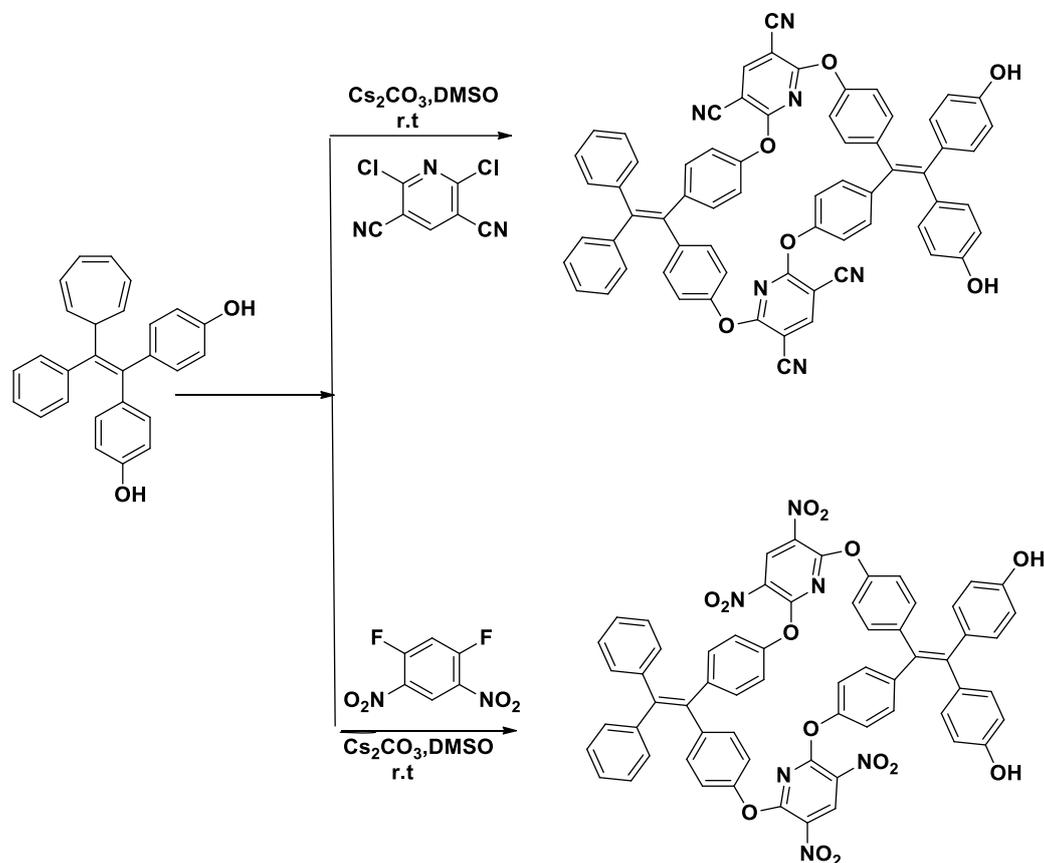


Figure 6. The synthesis of TPE-based Oxacalixarenes 1a and 1b.

### 3. Conclusions

This review article focuses on the latest advances, functionalities, synthesis, and architecture of calixarene-based macromolecular systems, as well as their topologies. The synthesis of new calixarene-based macromolecular structures with new functionalities and architecture is still a source of concern for researchers. The most popular identification methods are visual (colorimetric and photoluminescent). The versatility, absence or a low number of incorrect readings, high speed (the test is available in a minute or less), and portability are the main benefits of these techniques. The development of a covalently bonded substance or non-covalently bonded molecular complex between the electron-withdrawing nitro compound (analyte) and the electron-donating chemosensor is the central driving factor in the visual detection of nitroaromatic compounds (explosives) (reagent, sensor, or indicator). This reaction results in an extreme color, static or dynamic fluorescence quenching, and/or an improvement in the sensor's luminescence characteristics, or, in very rare cases, chemosensor photoluminescence enhancement (fluorescence).

In the future, researchers can design new calixarene-based chemosensors having high selectivity, ultra-sensitivity and can test their activity towards various classes of explosives.

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## Conflicts of Interest

The authors declare no conflict of interest.

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