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Chemosensors for detection of nitroaromatic compounds (explosives)

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The key types of low-molecular-mass chemosensors for the detection of nitroaromatic compounds representing energetic substances (explosives) are analyzed. The coordination and chemical properties of these chemosensors and structural features of their complexes with nitroaromatic compounds are considered. The causes and methods for attaining high selectivity of recognition are demonstrated. The primary attention is paid to the use of low-molecular-mass chemosensors for visual detection of explosives of this class by colorimetric and photometric methods. Examples of using photo- and chemiluminescence for this purpose are described. A separate section is devoted to electrochemical methods of detection of nitroaromatic compounds. Data published from 2000 to 2014 are mainly covered.
The bibliography includes 245 references.

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I. Introduction

The synthesis and practical use of chemosensors † for the detection of energetic compounds, including nitro-containing (aliphatic and aromatic) explosives is a promising line of analytical and synthetic (hetero)organic chemistry. During the last decade, considerable attention in the literature has been devoted to the 'electronic nose' concept, which is a type of analyzers detecting vapours in air or molecules in solutions by means of organic-inorganic sensing polymers or polymer composites with impregnated

† In this review, by chemosensor (chemical sensor) is meant a chemical reagent that reacts with the analyte to produce an easily detectable effect.

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one or numerous different-type (non-equivalent) sensors. These devices mimic the functions of the taste and olfactory organs of mammals (dogs,[1,2] more rarely, rats[3,4] or pigs[5]) or insects (usually, wasps‡ or bees§). Currently, some types of 'electronic noses' based on chemical sensor elements have already found real application for the search for explosives¶ and represent a serious alternative to sniffer dogs, as they approach the dog's limit of detection but are virtually free from the drawbacks inherent in the dog service.

The importance of the search and subsequent advancement of high-sensitivity chemosensors and the development and manufacture of effective materials for sensing elements of various 'electronic noses' is obvious from the fact that numerous publications are devoted to the synthesis of both individual chemosensors and polymer sensing materials and application of these materials for the detection of energetic compounds. Among these publications, mention should be made of several reviews[6–13] and monographs.[14–17]

This review is the first attempt to analyze the results of studies dealing with the use of single low-molecular-mass chemosensors, organic-inorganic polymeric materials and analytical reagents and indicators having small molecules as the active principle and being used for visual and/or electrochemical detection of nitroaromatic compounds (explosives). We mainly included data published from 2000 to 2014, while earlier papers are referred to only in those cases if the data they report are not covered in recent publications.

II. Visual detection of nitroaromatic compounds

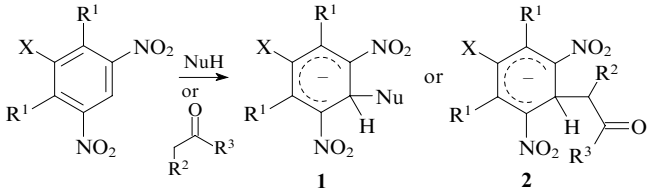
The visual methods used to detect nitroaromatic compounds are rapid, simple and reliable. They are subdivided into colorimetric (photometric) and photoluminescence-based methods.

1. Colorimetric methods

Colorimetric methods are based, most often, on irreversible colour change of various media containing nitroaromatic compounds under the action of chemical analytical reagents or indicator compounds. These fast and inexpensive methods are used most widely to detect 2,4,6-trinitrotoluene (TNT)† and, in most cases, they do not require special equipment, as they imply straightforward interpretation of the obtained result according to the 'Yes' or 'No' principle.

The chemical principle of detection of TNT and its derivatives is based on the fact that highly electrophilic nitroaromatic moieties react with nucleophiles to give intensely coloured Meisenheimer complex **1**, which is also called Jackson–Meisenheimer complex.[18] Most typically, the nicleophiles used are N- or O-centred;[18,19] however, examples of formation of similar complexes with S- and P-centred nucleophiles are also encountered in the literature.[18] Depending on the nature of the nucleophilic reagent and/or nitroaromatic compound, the colour of complex **1** is different, which may serve for identification (Scheme 1).

Scheme 1



R^1 = H, Me; X = H, NO_2; R^2, R^3 = H, Alk, Acyl, Ar; NuH are O-, S-, P-, C- and N-nucleophiles

The reactions with C-nucleophiles (*e.g.*, Grignard reagents or cyanide anion[18]) also give rise to coloured Meisenheimer complexes, while in the case of C-nucleophilic ketones, other complexes are formed, namely, Janovsky complexes **2**.[18]

The methods based simply on the reaction of nucleophiles with nitroaromatic analytes yielding the Meisenheimer or Janovsky complexes can find practical use for rapid analysis of soil samples for traces of TNT and its derivatives.[20,21] For example, N- or O-nucleophile-containing fragments were used by Spanish researchers[22] to design so-called 'smart materials' for TNT detection.

By the reaction of Au^{III} compounds (for example, $HAuCl_4 \cdot 3H_2O$) and hexaazacrown ether that contained aromatic rings and secondary amino groups, Indian researchers[23] obtained nano-sized gold-containing colorimetric chemosensors with the limit of detection of TNT of 155 fmol litre^{-1}.

Chinese authors[24] used the reaction of gold citrate nano-sized particles with ethylenediamine to fabricate nanosensors for visual (colorimetric) detection of 2,4-dinitrotoluene (2,4-DNT) and TNT in water with a sensitivity of down to 0.4 pmol litre^{-1}.

Also, noteworthy are the sensing materials described[25] by a US and Chinese research team. The materials were fabricated by photolithography on the surface of polymeric membranes, which were subsequently functionalized by chromogenic reagents, in particular, alkylamines. These materials served for colorimetric detection of TNT and 2,4-DNT vapours in air; the limits of detection ranged from 180 ppb to several ppt (ppb is a part per billion and ppt is a part per trillion).

Under similar conditions, picric acid forms coloured Meisenheimer complexes.[8]

Recently, a stable intermediate formed in the reaction of picric acid with diisopropylcarbodiimide in dichloromethane was detected. Spirocyclic product **3**, a stable Meisenheimer complex (Scheme 2), was isolated in the crystalline state and fully characterized.[26]

Yet another method for colorimetric detection of nitroaromatic compounds is based on non-covalent interactions, resulting in the reversible formation of intensely coloured π-complexes, or charge transfer complexes

‡ See American Chemical Society. *Trained Wasps May Be Used To Detect Bombs, Bugs, Bodies And More*. ScienceDaily, October 21, 2005; http://www.sciencedaily.com/releases/2005/10/051021120542. htm

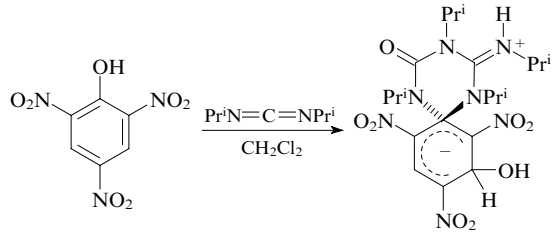
§ See Los Alamos National Laboratory. *Detecting Explosives With Honeybees: Experts Develop Method To Train Air Force Of Bomb-sniffing Bees*. ScienceDaily, November 29, 2006; http://www.sciencedaily.com/releases/2006/11/061128140820. htm

¶ See http://gs.flir.com/detection/explosives/fido and http://itar-tass.com/sport/854592

† Currently, TNT still remains the most widely used explosive present as a part of more than fifty explosive mixtures.[8]

(CTC),[27] between the aromatic nucleus of the (poly)nitroaromatic compound (charge acceptor) and donor molecules.

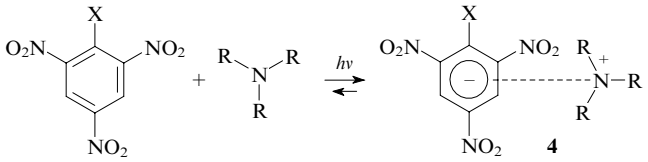
Scheme 2



3

As donors, it is possible to use polyaromatic compounds or Lewis and Brønsted bases, for example, halogens (most often, iodine),[28,29] aromatic amines (anilines[30]) and sterically hindered aliphatic amines (dicyclohexylamine). The coloured CTC **4** (Scheme 3) is formed upon partial charge transfer from the donor to the acceptor due to the overlap of the molecular orbitals with appropriate symmetry.

Scheme 3

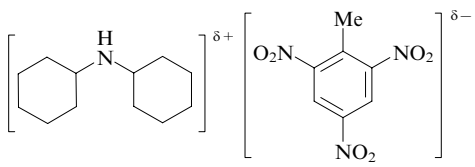


X = H, OH, Me; R = Alk

In this case, an intense charge transfer absorption band appears in the UV spectrum. Additionally, an estimation of the change in the CTC colour intensity, for example, by means of digital photography by analyzing the 'red–green–blue' (RGB) balance,‡ allows for quantitative analysis of the content of nitroaromatic compounds in various media.

The poly(vinyl chloride) polymeric matrix with impregnated dicyclohexylamine operates according to the same principle and can be used to detect down to 3×10^{-6} g cm^{-3} of TNT in air. When air containing TNT vapour is passed above the matrix surface, the polymer is coloured violet due to the formation of the donor–acceptor complex **5**. This material does not react with tetryl, picric acid, RDX or tetranitro-pentaerythritol.

Structure 5



5

‡ For example, in one study,[31] the authors successfully used just the iPhone digital camera.

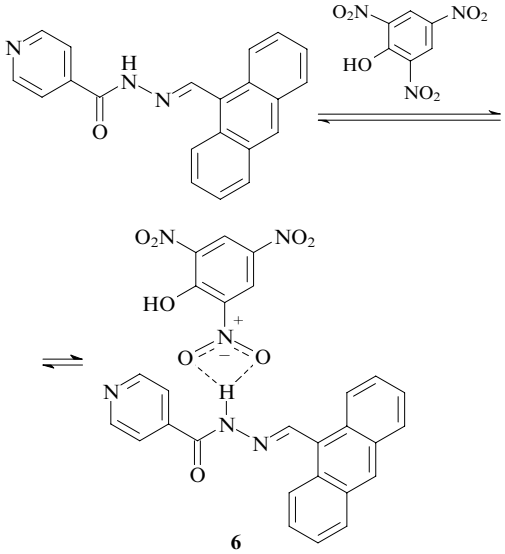
Recently, Chinese researchers[32] developed a highly sensitive colorimetric organic–inorganic nanosensor for the detection of TNT and its derivatives in aqueous solutions. For instance, the supramolecular clusters obtained upon aggregation of gold nanoparticles with 2,4,6-triamino-1,3,5-triazine (melamine) were destroyed upon the reaction with TNT and related compounds, which was accompanied by a colour change. The authors attributed this outcome to the formation of stable 'melamine (donor)–nitroaromatic analyte (acceptor)' complexes. Visually, one can see the colour change from grey-blue (inherent in the 'melamine–gold nanoparticle' complex) to red-brown (free gold nanoparticles), the limit of detection for TNT being 27 mmol litre^{-1}.

Phenothiazines can form stable intensely coloured CTC, for example, upon co-crystallization with nitroaromatic compounds.[33,34] In a recent publication,[35] US researchers observed an intensely coloured CTC comprising 10-methylphenothiazine and 1,3-dinitrobenzene in the solid phase. In addition, the film obtained by spraying a solution of 10-methylphenothiazine in polystyrene on a glass surface demonstrated a sensor response to nitroaromatic compounds in air; in the authors' opinion, this may be a prerequisite for the use of this compound for the visual detection of TNT.

Stable salts were found to form in the reaction of picric acid (see Scheme 3, X = OH)[36] in aprotic solvents with azacrown ethers and some azoles, for example, imidazole.[37] In this process, the NH-group nitrogen atom is protonated *via* transfer of the acidic proton from the phenol group of picric acid accompanied by partial charge transfer from the lone electron pair of the NH group to the π*-orbital of the nitro group.

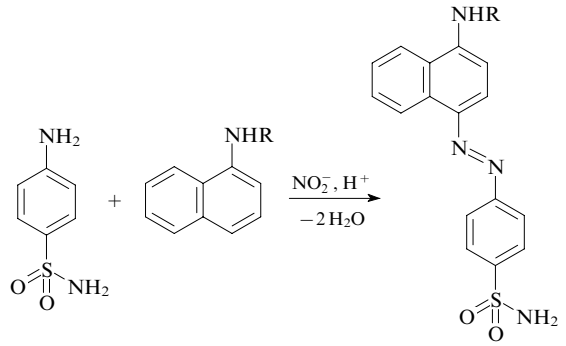
The NH groups of carboxylic acid amides and hydrazides are not protonated but they tend to form hydrogen bonds with the nitro groups of picric acid. For example, Chinese researchers described[38] the reaction of picric acid (PA) with the Schiff base obtained by condensation of isonicotinic hydrazide with anthracene-9-carbaldehyde. This yields molecular complexes **6** formed by hydrogen bonds; the structure of the complexes has been unambiguously proven by X-ray diffraction (Scheme 4).

Scheme 4



6

Scheme 5



R = Alk

7

The intense quenching of the Schiff base fluorescence in solution upon the addition of PA and the dramatic change in the colour of crystalline forms (from light yellow in the free state to bright red in complex **6**) were attributed by the authors to the change in the free base geometry upon the formation of a molecular complex in the presence of picric acid. Note that in solution, this reaction is reversible since it is not accompanied by (de)protonation of the NH groups in the starting hydrazone, as indicated by the results of titration using ^{1}H NMR spectroscopy.

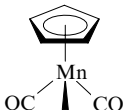
There are also known methods for colorimetric determination of TNT and its derivatives using inorganic reagents such as the Nessler reagent [potassium tetraiodomercurate(II)].[39] For example, a method for TNT determination in soil samples by the Nessler reagent with a sensitivity of down to 0.01 mg litre^{-1} was recently reported.[40]

Finally, aromatic nitro compounds (like nitramines but to a lesser extent) can undergo photo,[41] bio[42] and catalytic[43] degradation to give nitrites, which enter into the Griess colour reaction to give, for example, azo dye **7** (Scheme 5).[10]

In addition, the degradation of nitroaromatic compounds may afford nitrogen oxides, first of all, NO_2.[44] Nitrogen(IV) oxide can be detected upon the formation of intensely coloured nitrosonium[45] or nitronium[46] π-complexes with (poly)aromatic compounds (for example, calix[4]arenes, triptycenes[47] and so on) or organometallic complexes (for example, ferrocene and cymantrene).

Indeed, cymantrene (**8**) impregnated into divinylstyrene polymer matrix detects trace amounts of NO_2, which are evolved from surfaces contaminated by nitrotoluene and dinitroaromatic compounds (taken as TNT models), upon contact with the polymer. This results in intense colouring of the polymer film with the absorption maximum (λ_{max}) at 680 nm.[48]

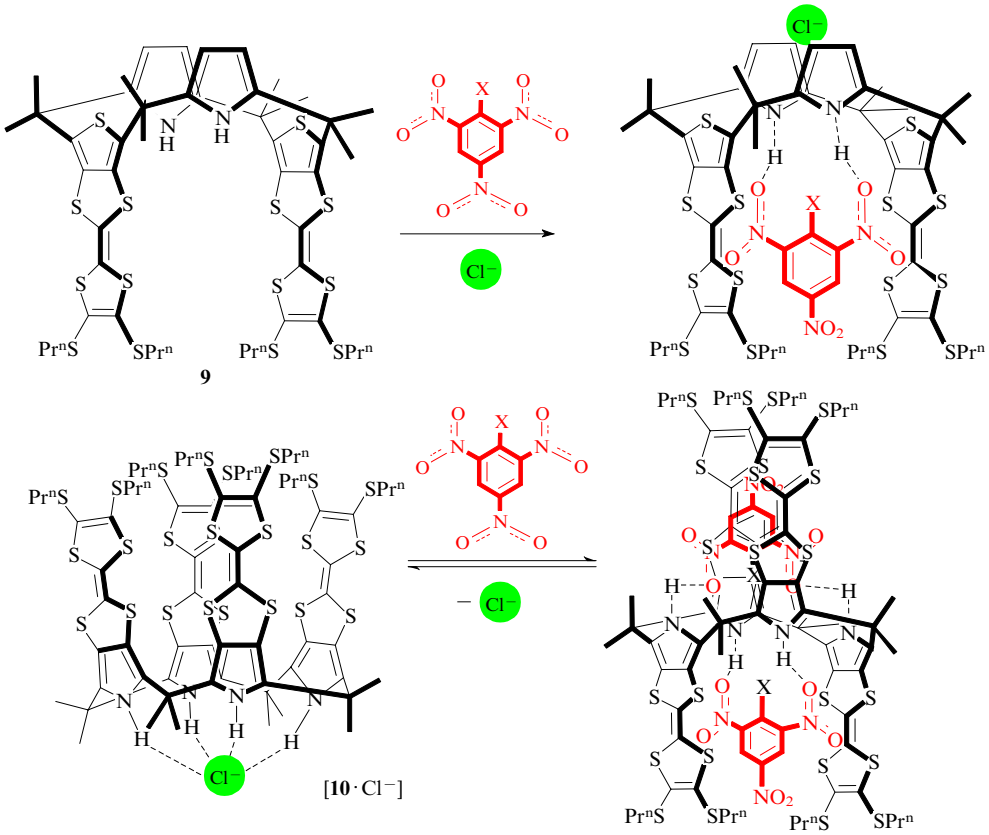
Structure 8



8

Despite the relatively ready synthetic accessibility of indicator compounds and reagents used for the colorimet-

Scheme 6



X = H, OH

ric detection of nitroaromatic explosives, the method suffers from low selectivity and, hence, a large number of false-positive results.[6–8] Hence, for more specific operation, it is recommended either to use chemical grafting of chemosensor (reagent, indicator) molecules on the surface of organic-inorganic matrices in order to obtain an extended contact surface with the target analyte or to increase the chemosensor selectivity by chemical tailoring to a particular nitroaromatic compound.

An example of the latter approach is the fulvalene-based chemosensor described by Sessler and co-workers.[49] In order to detect picric acid and 1,3,5-trinitrobenzene (TNB), they used bis(tetrathiafulvalenocalix[2]thiophene[2]pyrrole) (**9**) and tetrakis(tetrathiafulvalenocalix[4]-pyrrole) (**10**) existing in the 1,3-*alternate* conformation (Scheme 6).

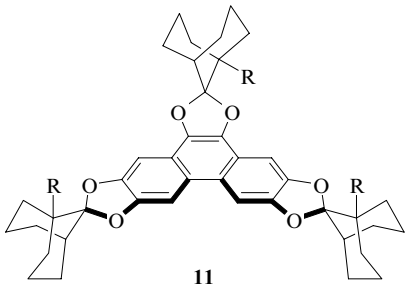
Titration of solutions of sensors **9** and **10** in chloroform with picric acid, TNB and TNT induced intense colouring. This was attributed by the authors to the formation of a sandwich inclusion complex through the π–π interaction of the electron-deficient nitroaromatic compounds with parallel arrangement of the thiophene moieties of fulvalene and additional hydrogen bonding between the pyrrole NH groups of calix[4]pyrrole or calix[2]thiophene[2]pyrrole and the NO_2 or OH oxygen atoms.

The structure of complex [**9**·TNB] was confirmed by X-ray diffraction data.[49] Note that the addition of chloride ions to the complexes of calixpyrrole **10** with nitroaromatic compounds leads to displacement of the nitroaromatic compound from the cavity and 'locking' of sensor **10** in the inactive *cone* conformation as the complex with the Cl^- anion. This complex is no longer capable of further transformations induced by picric acid, TNT or TNB. Meanwhile, compound **9** can react with nitroaromatic compounds both in the presence and in the absence of Cl^- anions.

2. Photometric detection based on the change in the transmittance coefficient of a receptor layer

In 2005, Waldvogel and co-workers[50] described an effective synthetic receptor for encapsulation of (hetero)aromatic substrates based on triphenyleneketal **11**; data on the structure of **11** were gained by X-ray diffraction analysis and quantum chemical calculations.

Structure 11



11

A later study by Waldvogel's team[51] presents an effective device based on a quartz ring microresonator with the surface modified with triphenylene ketal **11**, which encapsulates TNT within the receptor cavity. The device detects TNT in air in concentrations down to 5 ppb, apparently due to the formation of TNT–triphenylene inclusion π-complexes (Fig. 1).

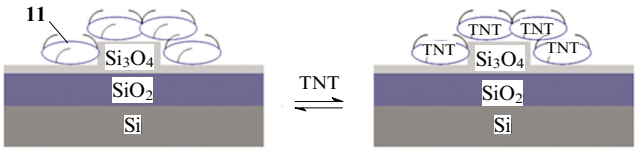
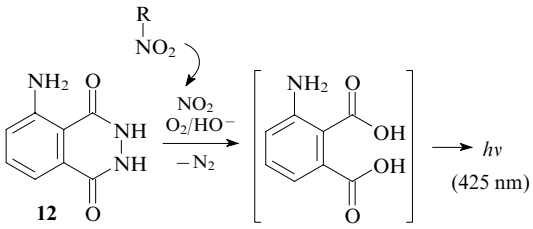


Figure 1. Schematic view of the operation of a microresonator with deposited triphenylene ketal **11**.[51]

3. Chemiluminescent detection

The chemuluminescent detection of explosives is based on the oxidation of luminol (**12**) in the presence of nitrogen dioxide formed upon (photo)degradation of nitro(aromatic) compounds (see Ref. 52, p. 173). This method proved useful, first of all, for the detection of aliphatic nitro compounds and TNT and its derivatives (Scheme 7).[53, 54]

Scheme 7



The detection of nitroaromatic compounds using bio- and immunosensors followed by chemiluminescent recording of the sensor response is also fairly popular.[55–57]

4. Photoluminescent detection

Nitroaromatic compounds are the most typical analytes for photoluminescence methods owing to the ability to form stable π-complexes with polycyclic (hetero)aromatic compounds. The planar structure and the presence of electron-withdrawing nitro groups in the aromatic ring, which lowers the energy of vacant π*-orbitals, makes nitroaromatic compounds capable of accepting electrons upon donor–acceptor (most often, π–π) interactions with electron donors. The oxidative properties of nitroaromatic compounds are enhanced with increase in the number of nitro groups: for example, the reduction potentials determined by galvanic measurements against the hydrogen electrode decreases in the series nitrobenzene (NB) (21.15 V), 2,4-dinitrotoluene (20.9 V), 2,4,6-trinitrotoluene (20.7 V).[58]

The luminescent detection of nitroaromatic compounds is based on the change of luminescence properties, namely, the fluorescence (or phosphorescence) quantum yield or the excited state lifetime, of the sensor donor molecule upon complete or partial electron or energy transfer after the contact with a nitroaromatic compound. In the general case, this is the inverse process with respect to the colorimetric detection. On contact with the photoluminescence indicator (chemosensor) molecule, the analyte molecule reduces the intensity of light emitted by the indicator. The Stern–Volmer equation (1) is the mathe-

matical expression describing the fluorescence quenching. The emission intensity (I_0) in the absence of an analyte is fairly high (this is a necessary condition), while the emission intensity (I) in the presence of an analyte that quenches the fluorescence depends on the quencher concentration ([Q]).

$$I_0/I = (1 + K_A [Q])(1 + k_q \tau_0 [Q]) \quad (1)$$

The contribution of so-called static quenching, which occurs *via* the formation of a donor–acceptor complex between the sensor in the ground state and the nitroaromatic compound, is characterized by the binding constant K_A.

If the sensor molecule exists in the excited state, dynamic quenching is due to the Förster resonance energy transfer (FRET) or the Dexter exchange (called also collision) transfer. The contribution of this type of quenching to the change in the fluorescence intensity is determined by the lifetime of the photoluminescence excited state of the indicator molecule upon photoexcitation (τ_0), because the dynamic quenching is possible only during this period, and by the reaction rate (k_q) between the analyte molecule and the indicator molecule. In most cases, the Stern–Volmer quenching constant (K_{SV}) is determined by the contribution of the type of quenching that prevails in the particular case.

In the case of both static and dynamic quenching, fluorescence is attenuated due to the electron transfer from the indicator molecule existing in either ground or excited state to the nitroaromatic molecule in the ground state. A simple chart of fluorescence quenching by nitro compounds is shown in Fig. 2.

Upon the photoexcitation of the sensor molecule, an electron passes to a molecular orbital with a higher energy, namely, the lowest unoccupied molecular orbital (LUMO). On contact with the nitro compound, the electron from the LUMO of the sensor can migrate to the LUMO of the nitroaromatic compound, which results in fluorescence quenching. The energy difference between the sensor LUMO and the nitroarene LUMO is the thermodynamic driving force (DF) of fluorescence quenching (see Fig. 2).

Several mechanisms can serve for photoluminescent detection of nitroaromatic compounds. They are all based on chemosensor photoluminescence quenching in the presence of a nitroaromatic compound, for example, due to the photoinduced electron transfer (PET), complete or partial electron transfer from the donor [chemosensor (indicator) molecule] to the acceptor (nitroaromatic compound). This process is accompanied by the formation of non-fluorescent ground-state molecular complex, which may be ascertained using UV-spectroscopy data. If the chemosensor molecule reacts with the nitroaromatic compound in the excited state, so-called dynamic quenching tales place due to Förster or Dexter energy transfer. One more method of photoluminescent detection of nitroaromatic compounds is based on the formation or destruction of excimers (usually, between the chemosensor molecules) and exciplexes (between the chemosensor and the analyte). Finally, in the case of organometallic chemosensors, photoluminescence quenching can be due to processes related to photoinduced charge transfer (PCT) (see a review [59] and references cited therein).

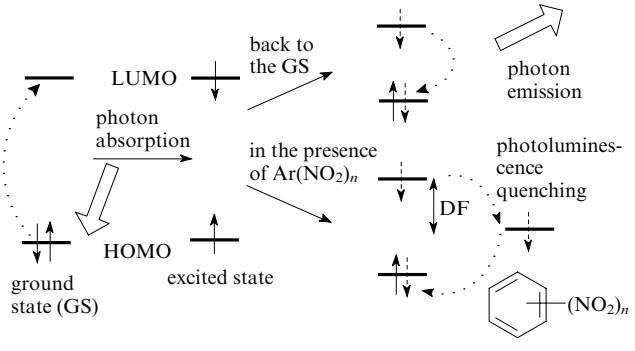


Figure 2. Fluorescence quenching mechanism on contact of the chemical sensor and nitro compounds.

In most cases, the static fluorescence quenching prevails and, therefore, it is used more often for luminescent detection of nitroaromatic compounds. The presence of static quenching is indicated first of all by high values (10^3 mol litre^{-1} and higher) of constants K_A of complexation (quenching) between nitroaromatic compounds and photoluminescence sensor molecules [most often, electron-excessive (hetero)aromatic compounds]. The lifetime of the excited state of photoluminescence of chemosensors remains unchanged upon increase in the concentration of the nitroaromatic compound.

a. Quantum chemical calculations and X-ray diffraction data

The data of quantum chemical calculations provide the primary information on the possible structure of the molecular complex chemosensor–nitroaromatic compound and can be used to estimate the effect of steric and electronic factors on the stability.

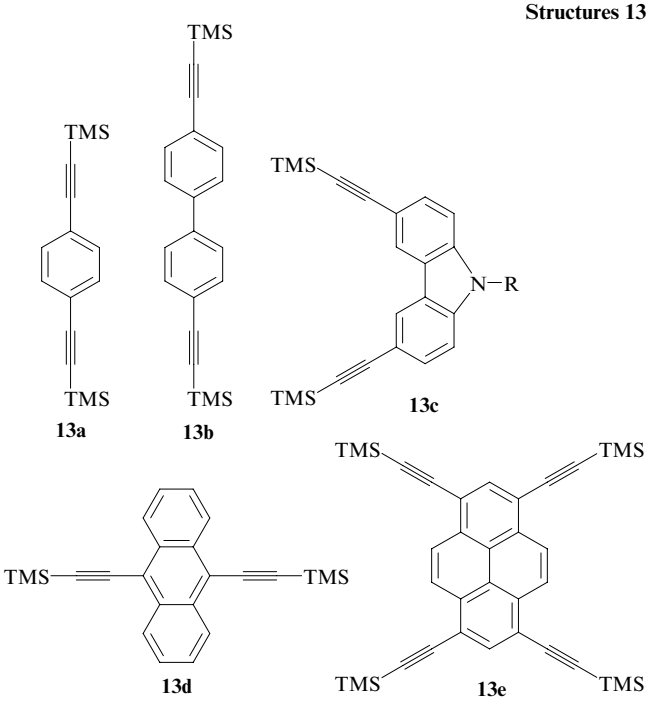
Wen *et al.*[60] used density functional theory (DFT) quantum chemical calculations (DMol 3 package: Materials Studio 3.1) to estimate the electrostatic and steric aspects of complexation of 2,4,6-trinitrotoluene with triphenylene. By means of this algorithm, the minimum energy state characterized by a stacked structure with a $\sim$3.5 Å distance between the molecules was calculated for the complex.

According to the calculations of electrostatic potentials for TNT and triphenylene, in the free state the negative charge is concentrated at the centre of the triphenylene molecule. The $\pi-\pi$ interaction results in almost complete migration of the negative charge from the triphenylene molecule to TNT, which attests to the formation of a stable donor–acceptor complex.[60]

Indian authors [61] observed intense fluorescence quenching of poly(hetero)aromatic compounds (benzene, biphenyl, carbazole, anthracene and pyrene) modified by trimethylsilylacetylene moieties — chemosensors **13a–e** — in organic solvents in the presence of nitroaromatic compounds with the quenching constant (K_{SV}) of up to 2×10^5 litre mol^{-1} (for picric acid).

The most effective compounds, 9,10-bis(trimethylsilylethynyl)anthracene (**13d**) and 1,3,6,8-tetrakis(trimethylsilylethynyl)pyrene (**13e**), in thin films on the surface showed intense fluorescence quenching in the presence of vapours of mononitro compounds: 4-nitrotoluene (up to 25% in 120 s), nitrobenzene (50% in 120 s) and nitrophenol (46%). In all cases, the less efficient chemosensor

Structures 13



TMS is trimethylsilyl; R = Alk

13e (quantum yield of 10.4% *versus* 16.4% for compound **13d**) was more prone to detect nitro compounds in the vapour phase than in solutions.

The DFT quantum chemical calculations of the presumptive structure of the complexes of **13d**,**e** with picric acid (Gaussian 03 with the MPWB1K hybrid functional[62] and the 6-31G* basis set) showed that the formation of complex [**13e**·PA] is energetically preferable (the formation energy is 16.32 kcal mol^{-1} *versus* 14.09 kcal mol^{-1} for complex [**13d**·PA]), which is due, in the authors' opinion, to steric hindrance. The bulky trimethylsilyl substituents at the periphery of the pyrene ring of chemosensor **13d** prevent the access of the nitroaromatic compound, which hampers the formation of the π–π-complex (Fig. 3).

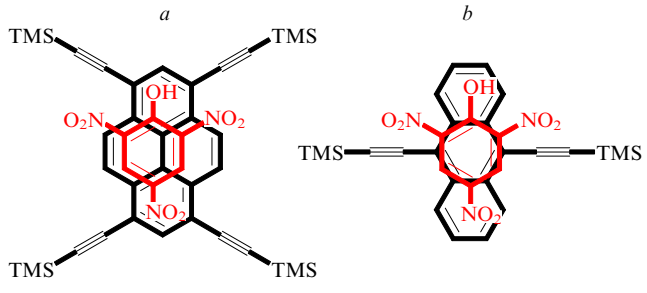
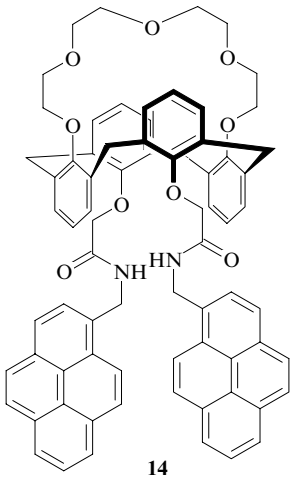


Figure 3. Presumptive structures of complexes [**13e**·PA] (*a*) and [**13d**·PA] (*b*).

Sessler and co-workers[63] described effective chemosensor **14**, which is formed by calix[4]arene modified by pyrene residues at the periphery of the cage. In particular, X-ray diffraction data (Fig. 4) and DFT quantum chemical calculations (Gaussian 03: MPWB1K, 3-21G* basis

Structure 14



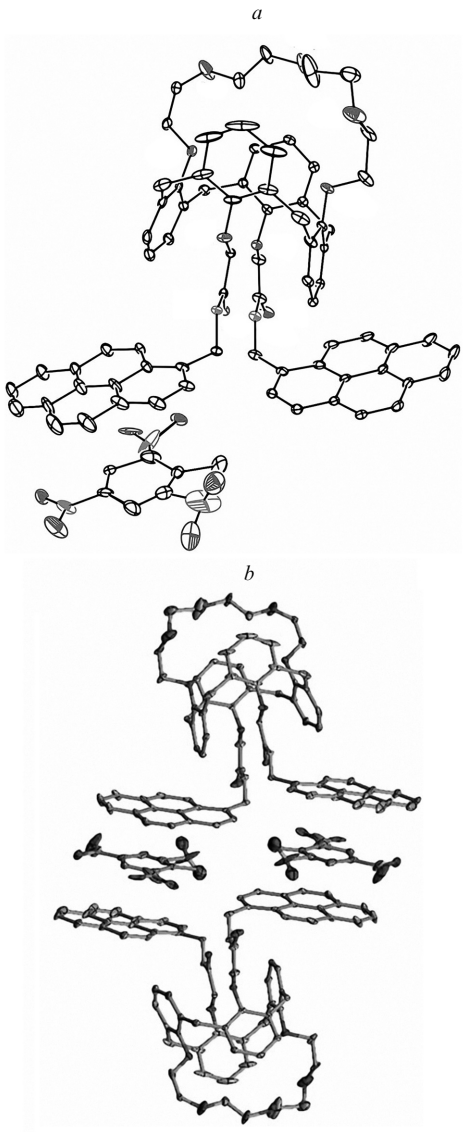


Figure 4. X-Ray diffraction data for molecular complex [**14**·TNT] (*a*) and for intermolecular interaction between two neighbouring pyrene moieties and TNT (*b*).[63]
The hydrogen atoms and solvent molecules are omitted for simplicity.

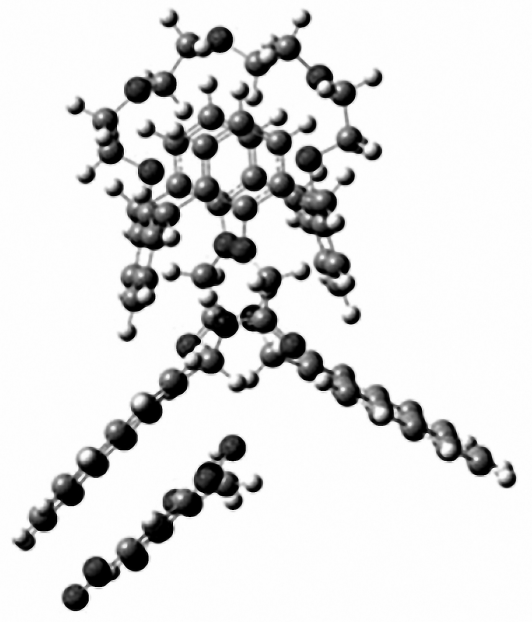


Figure 5. Optimized structure of molecular complex [**14**·TNT] from DFT quantum chemical data.[63]

set) of the optimal structure of the molecular assembly of pyrenylcalixarene and nitro compounds demonstrated the possibility of the formation of π-complexes between the pyrene moiety and nitrobenzene or TNT (Fig. 5).

b. Polynuclear aromatic compounds

According to the commonly accepted views, the sensing properties of polymeric sensors are enhanced as compared with monomers. This is caused by a larger number of receptor groups in the effective chain of conjugation of the macromolecule in the polymeric chemosensor compared to analogous monomeric receptors.[64] This effect is called amplification; one of the founders of this theory is Swager.[65]

However, in recent decades, fluorescent chemosensors based on 'small' molecules (for example, monomers, generation 1–2 dendrimers and short oligomers) have been successfully competing with fluorescent polymeric chemosensors. The key advantages of these molecules include the possibility of targeted synthesis based on quantum chemical calculations and mathematical modelling for detection of substances of a particular type, relative synthetic accessibility (a small number of synthetic steps), realization of various types of fluorescence quenching, and, hence, applicability to the detection of almost any type of known nitroaromatic and other nitro explosives. A fundamental difference between the 'small' molecules and conjugated polymers is the absence of effective exciton migration (due to the absence of an effective conjugation chain). It is also noteworthy that on contact with nitroaromatic compounds, fluorescent polymers show mainly the static fluorescence quenching, due to multiple intermolecular interactions between the monomeric units of the polymer and analyte molecules *via* the formation of molecular complexes. In the conjugated polymer, the exciton migration (the so-called molecular wire effect[66, 67]) along the polymer chain (or, more rarely, through space) to the site of the contact with the nitro compound accelerates quenching. The efficiency of detection of nitroaromatic compounds in the conjugated polymer is directly related to the polymer chain growth, as numerous receptor groups are generated but the polymer still behaves as a single molecule.

Conversely, in the case of 'small' molecules, a single analyte molecule reacts with the whole sensor molecule (rather than with its part); therefore, the efficiency of detection of nitroaromatic compounds by 'small' molecules depends on the concentrations of the sensor and the analyte (in this case, a nitroaromatic compound). One way to increase the efficiency is to place the 'small' molecules into organic or inorganic polymeric matrices to enhance the complexation with the analyte (nitroaromatic compound) or to induce the intermolecular through-space migration of the exciton. In this case, the nanowire effect will be implemented in the ideal case.[68]

Since nitroaromatic compounds have a planar structure and high π-electron deficiency, they are expected to predominantly form π-complexes with annulated polyaromatic compounds, for example, triphenylene and its isosteres, for instance, naphthalene, phenanthrene, pyrene, dibenzoanthracene, helicenes and so on (Fig. 6). Additionally, one can expect the formation of hydrogen-bonded assemblies through involvement of functional groups at the chemosensor periphery (*e.g.*, hydrogen bond donors) into the interaction with nitroaromatic analytes and inclusion compounds.

It can be seen in Fig. 6 that the triphenylene molecule is an isostere of 1,3,5-trinitrobenzene and its derivatives. In the most typical case, triphenylene forms stable

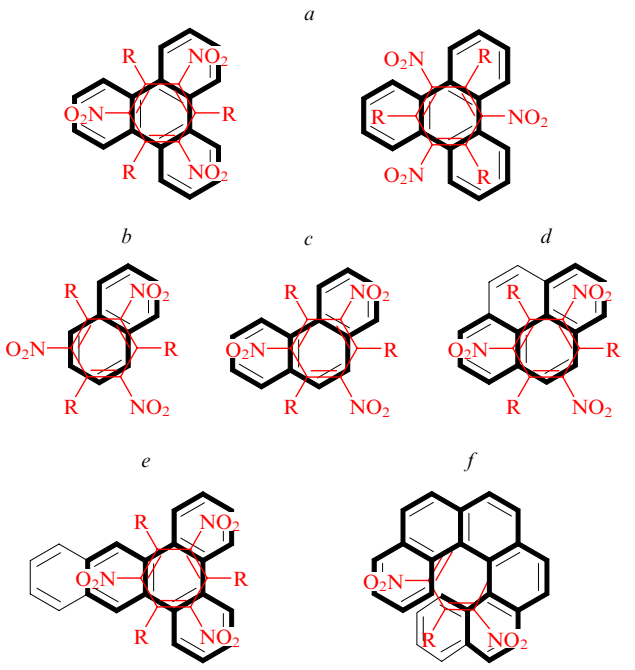


Figure 6. Structures of molecular complexes formed by nitroaromatic derivatives with polynuclear compounds: triphenylene (*a*), naphthalene (*b*), phenanthrene (*c*), pyrene (*d*), hexahelicene (*e*) and dibenzo[*a*,*c*]anthracene (*f*).

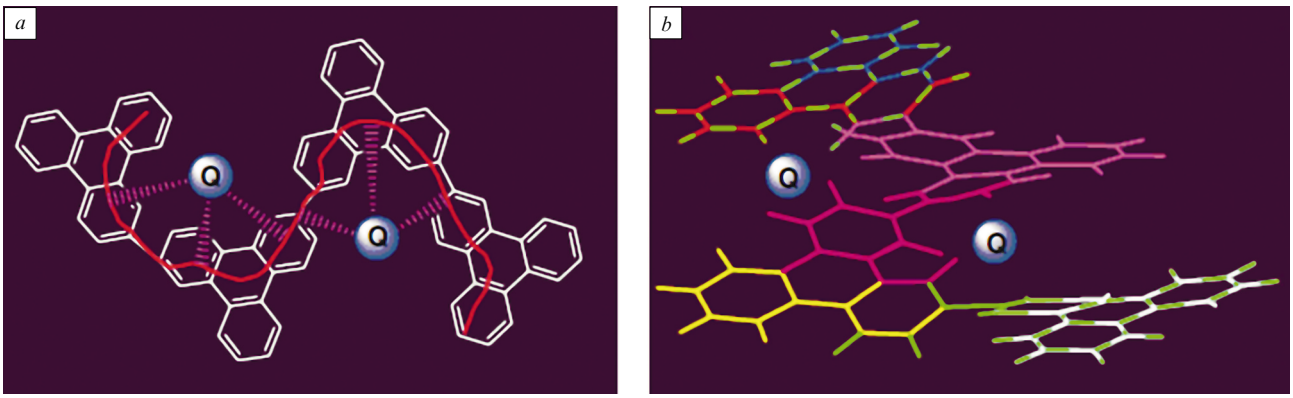
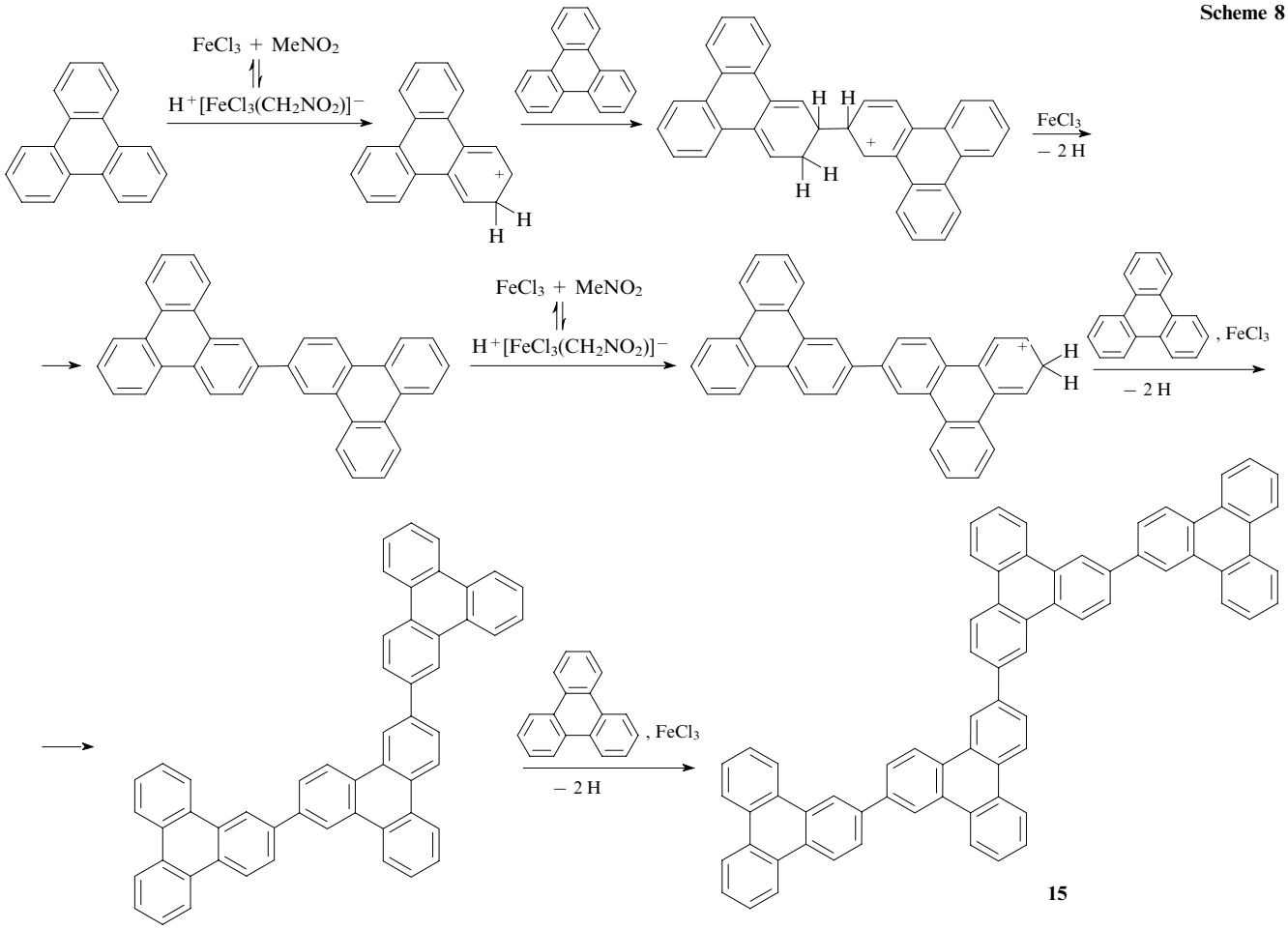


Figure 7. Presumptive structure of the donor–acceptor complex between oligotriphenylene **15** and nitroaromatic compounds (Q): top view (*a*) and side view (*b*).[71]

donor–acceptor complexes with polynitroaromatic compounds through intermolecular π–π charge transfer, which is confirmed by a large array of published data. For example, co-crystallization of triphenylene and TNB from nitrobenzene gives rise to a non-fluorescent non-centrosymmetric donor–acceptor exciplex with an alternating parallel arrangement of molecules[69] with distances between the donor and acceptor layers of 3.36 and 3.39 Å, which is typical of most donor–acceptor complexes.[70] The authors noted that a non-centrosymmetric space group is unusual for a donor–acceptor complex and attributed this to C_3 symmetry of the molecule.

Unsubstituted triphenylene has a rather low luminescence quantum yield (4%); therefore, it cannot be used for

Scheme 8



photoluminescent detection of nitroaromatic compounds. However, the efficiency of chemosensors based on triphenylene can be much increased by simple modification, for example, by increasing the contact surface with the analyte.

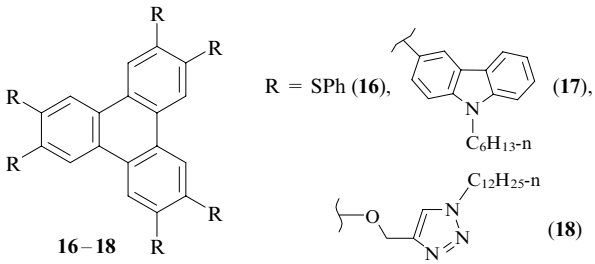
Thus by chemical and electrochemical oligomerization of triphenylene, Liao *et al.*[71] obtained oligotriphenylene **15**, that was formed as photoluminescent nanofibres 50 to 200 nm in diameter. In aqueous solutions and in organic solvents in the presence of nitroaromatic compounds, static quenching of its photoluminescence was observed (the chemosensor photoluminescence lifetime remained invariable upon an increase in the concentration of nitro compounds), the Stern–Volmer constants being of up to 10^5 litre mol^{-1}. In the authors' opinion and according to molecular dynamics calculations (Chem3D Ultra8.0), the tris(triphenylene) moiety forms a helical structure and, upon the contact with a nitroaromatic compound, it promotes the formation of CTC with encapsulation of the nitroaromatic compound in the oligotriphenylene cavity (Fig. 7, Scheme 8).

On the other hand, during vacuum sublimation, the monomeric triphenylene formed micro- or nanocrystalline fibres depending on the conditions; their scanning electron microscopy (SEM) images are shown in Fig. 8.[72] In the presence of nitrobenzene vapour, these fibres produced a stable photoluminescence sensor response (photoluminescence quenching) or electrical response (change in the conductivity).

A chemical modification of the triphenylene molecule may enhance its affinity to nitroaromatic analytes and/or serve as a sort of tuning of its photophysical characteristics. Li *et al.*[73] observed intense fluorescence quenching of 2,3,6,7,10,11-hexakis(phenylsulfanyl)triphenylene (**16**) in the presence of nitrobenzene. The formation of a stable donor–acceptor inclusion complex with the parallel arrangement of the aromatic nuclei of triphenylene **16** and nitrobenzene (the structure of the complex was proved by X-ray diffraction data) is, in the authors' opinion, a prerequisite for the use of this compound as a chemosensor for photoluminescent detection of polynitroaromatic compounds.

The introduction of heteroaromatic substituents into the periphery of the triphenylene nucleus can, in some cases, not only enhance its susceptibility to donor–acceptor interaction with nitroaromatic compounds by increasing the electron excess on the triphenylene moiety but also benefit the photophysical characteristics of the chemosensor (*e.g.*, increase the quantum yield) *via* supramolecular effects (*e.g.*, formation of stacked structures — excimers).

Structures 16–18



Indeed Bhall *et al.*[74] used chemosensors based on triphenylene functionalized by heterocyclic substituents to detect TNT and its derivatives. The introduction of bulky carbazole substituents adds to the system of conjugation in the resulting molecule; however, the quantum yield for chemosensor **17** decreases as the formation of excimers is hampered. A 1-dodecyl-1,2,3-triazole moiety attached to the periphery of the triphenylene core (chemosensor **18**) increases the quantum yield and, hence, increases the efficiency of detection of nitroaromatic compounds, because the dipole–dipole and π–π interactions between the 1,2,3-triazole substituents promote the formation of stacked structures in the solid state and in non-polar solvents.[75]

Unlike unsubstituted triphenylene, pyrene is a more widely used fluorescent label due to higher quantum yield (34%). It also tends to form donor–acceptor complexes (*via* π–π interactions) with electron-deficient compounds, including polynitroaromatic ones.[76] Goodpaster and McGuffin[77] studied quenching of the fluorescence of free pyrene in the presence of nitroaromatic compounds as an indirect method for photoluminescent detection of TNT and its derivatives in combination with gas chromatography/mass spectrometry analysis.

Chen *et al.*[78] described the use of 1-bromopyrene (**19**) and (*E*)-1,2-di(pyren-1-yl)ethene (**20**) for photoluminescent detection of nitroaromatic compounds. Despite the presence of a heavy bromine atom, which usually

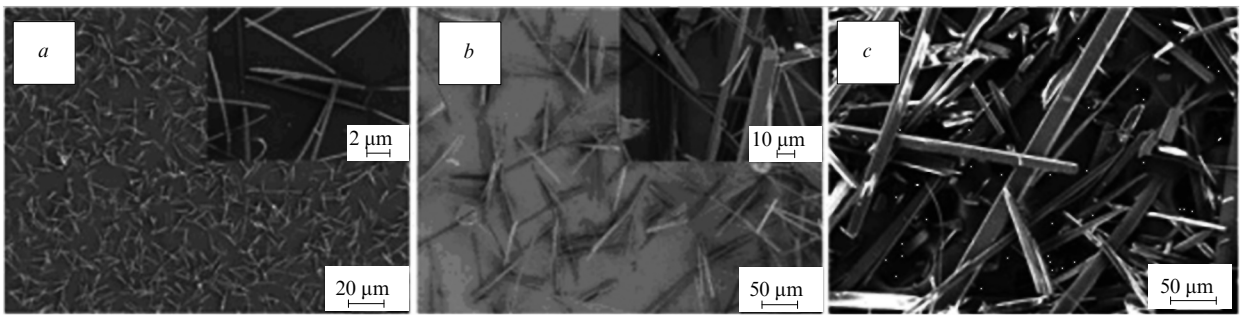
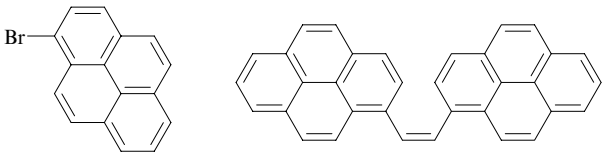


Figure 8. SEM images of the triphenylene nanocrystals formed during vacuum sublimation under various conditions: 180 °C, 5 min (*a*); 180 °C, 30 min (*b*) and 200 °C, 30 min (*c*).[72]
The insets in figures *a* and *b* show the same images on enlarged scale.

decreases the fluorophore quantum yield, 1-bromopyrene showed a more intense photoluminescence quenching in DMF in the presence of TNT and its derivatives with the Stern–Volmer constants of $(1-3)\times10^3$ litre mol^{-1}. According to the authors, dipyrenylethene **20** did not exhibit a substantial photoluminescence quenching under similar titration conditions.[78]

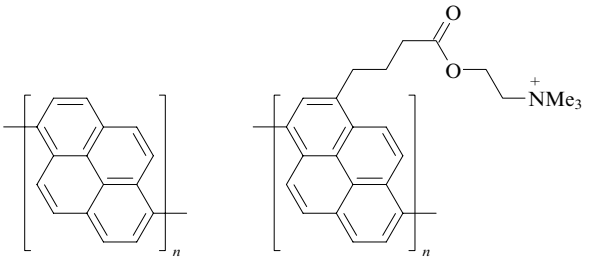
Structures 19, 20



19 **20**

Like triphenylene, pyrene can form oligomers under electropolymerization conditions. Chinese researchers[79] synthesized oligopyrenes **21a** containing 3 to 6 monomer units. In organic solutions and in the solid state, in the presence of TNT and its derivatives, these oligopyrenes showed a higher affinity to nitroaromatic compounds (more intense photoluminescence quenching) than the pyrene monomer. The authors attributed this to the 'molecular wire' effect.

Structures 21



21a **21b**

$n = 3-6$

Later, the same group of authors reported[80] water-soluble forms of oligopyrenes **21b**, which showed, in the presence of organic surfactants, static photoluminescence quenching with the Stern–Volmer constants of up to 5.30×10^5 litre mol^{-1} and the limit of detection of TNT of about 7.0×10^{-8} mol litre^{-1} (70 ppb). The authors attributed this fact to the formation of pseudo-micelles of oligopyrene **21b** in the presence of surfactants, inducing an increase in the quantum yield from 2.4% (in water) to 70% (in water with a surfactant).

Owing to its intense photoluminescence, the monomeric pyrene can be used in the design of effective sensing materials by being grafted as a photoluminescent label to organic or inorganic polymeric supports without being involved in the conjugation system of this material. The change (quenching) of the material photoluminescence occurs, in this case, only due to a change in the photoluminescence of the pyrene moieties upon the contact with nitroaromatic analytes (so-called extrinsic fluorescent probes[81,82]). For example, the introduction of 1-aminomethylpyrene moieties into the alternating copolymer of maleic anhydride and octadec-1-ene allows the resulting

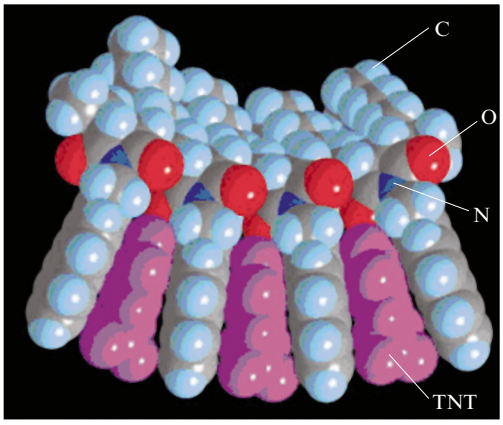
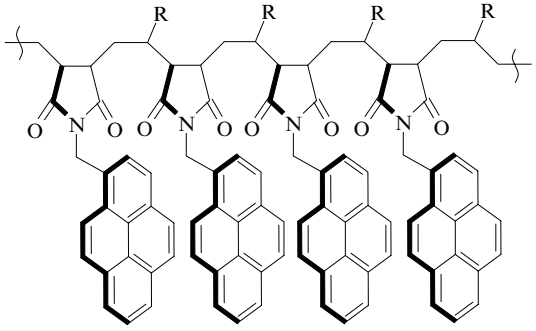


Figure 9. Interaction with TNT vapour of pyrene groups located at the periphery of the alternating copolymer of maleic anhydride and octadec-1-ene (**22**).[83]

material **22** to detect nitroaromatic compounds in solutions and in the solid state in polymeric films (Fig. 9). This is manifested as intense quenching of the fluorescence of polymer **22** in the presence of 2,5-dinitrobenzonitrile used as a TNT model. The formation of a stable donor–acceptor complex between pyrene and nitroaromatic compounds is confirmed by the new CTC absorption band at 430 nm in the UV spectra of these reagents in solutions.

Structure 22



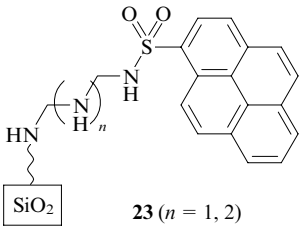
22

R = n-$C_{16}H_{33}$

In the case of thin films, the polymer fluorescence is quenched almost immediately in the presence of 2,5-dinitrobenzonitrile, which is probably caused by the formation of pyrene excimers in the solid state.[83]

The reaction of aliphatic polyamine residues (triethylenetetramine, diethylenetriamine and so on) pre-grafted onto a matrix surface with pyrene-1-sulfonic acid gave molecular monolayers on the glass matrix surface comprising pyrene moieties (structure **23**). These chemosensors responded to the presence of 2,4-DNT and TNT in solutions by reversible fluorescence quenching with detection limits of 5.49×10^{-11} and 7.14×10^{-12} g ml^{-1}.[84] The quenching intensity and, hence, the material sensitivity proved to be inversely proportional to the length of the polyamine linker (n).

Structure 23



23 (n = 1, 2)

Pyren-1-ylbutanoic acid incorporated in a polymeric membrane obtained by copolymerization of cellulose triacetate with isodecyl diphenyl phosphate is able to detect TNT and 2,4-DNT in concentrations of down to 2 mg litre^{-1} (based on quenching of pyrene fluorescence)[85] upon contact with air containing vapours of these analytes or other nitro explosives. The authors demonstrated that the material sensitivity is determined by the membrane permeability, which governs the active mass exchange area. It was also shown that the preliminary removal of air, which contains oxygen able to quench the pyrene fluorescence, from the membrane by nitrogen purging enhances the sensor response to vapours of nitro compounds.

It was demonstrated that unsubstituted monomeric pyrene can efficiently detect vapours of nitro compounds at a femto- or nanomolecular level[86] by being used as a fluorescent indicator additive to polyaromatic conjugated polymers (for example, polystyrene). In the presence of nitroaromatic compounds, the fluorescence of polystyrene nanofibres containing monomeric pyrene is intensely quenched (by >50% in 6 min). The authors attributed this fact to π–π interaction between the benzene side groups of polystyrene and the pyrene molecules, which prevents self-quenching of the polymer fibres upon aggregation. The close contact of the pyrene molecules with polystyrene phenyl substituents (Fig. 10) creates conditions for effective exciton migration between the aromatic systems owing to the 'molecular nanowire' effect.[65]

Using a similar approach, another Chinese research team[87] manufactured photoluminescent fibres (nanonet) by an electrospinning procedure based on graphene oxide, polyvinylpyrrolidone, aminopropyloxytriethoxysilane and pyrenecarboxylic acid as the photoluminescent label and/or the receptor group. Owing to the large active mass exchange area, in the presence of 10 ppb of TNT, the material demonstrated a 81% photoluminescence quenching at room temperature in 540 s. Apart from the formation of non-fluorescent sandwich complexes between the pyrene moieties and nitroaromatic analytes (PET fluorescence quenching), the key influence on the pyrene photoluminesce is made by quenching due to FRET between the pyrene fluorophores and the Meisenheimer complexes that are formed in the reaction of primary amines and TNT derivatives.

The polymer produced by polycondensation of polyethyleneimine with pyren-1-ylbutanoic acid has analogous properties. In aqueous solutions in the presence of ⩾33 ppt of TNT or tetryl, PET and FRET quenching of the pyrene photoluminescence is observed.[88] US researchers[89] described a sensing material obtained by deposition of aminoalkyltrimethoxysilane on the surface of quartz optical fibres followed by reaction of the terminal amino

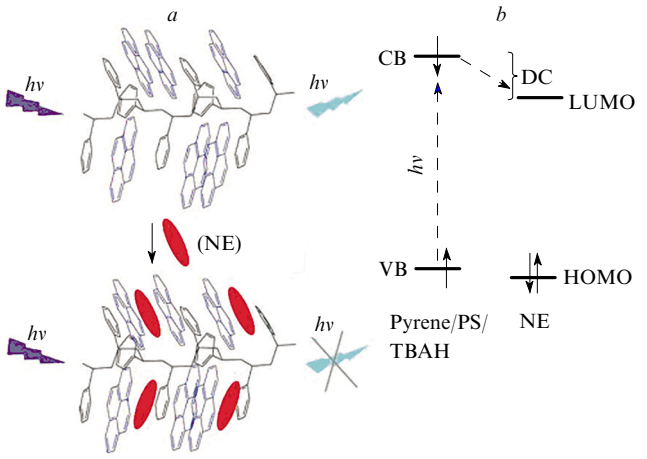
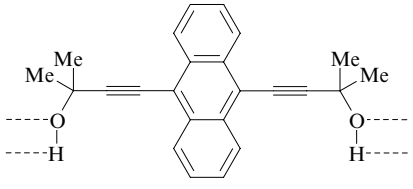


Figure 10. Interaction of pyrene-doped polystyrene (PS) nanofibres with nitroaromatic molecules (nitro explosives, NE) in the gas phase (*a*) and diagram of electron transitions (*b*).[86]
VB is the valence band, CB is the conduction band, TBAH is tetra-n-butylammonium hydroxide.

groups with perylene-3-sulfonic acid. In aqueous solutions in the presence of TNT (in a concentration of several ng m^{-3}), fluorescence quenching of the perylene chromophore was observed.

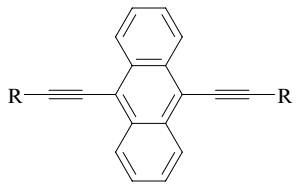
Along with the formation of excimers or exciplexes, owing to the π–π interaction between the pyrene molecules and between the pyrene and the polymeric matrix, supramolecular polymeric materials are used in some cases for effective detection of nitro explosives. These materials are formed with the participation of hydrogen bonds between substituents at the periphery of monomolecular polyaromatic fluorophores. For example, Indian researchers utilized 3-hydroxy-3-methylbut-1-ynyl-[90] and 3,5-bis(carboxyphenyl)ethynyl-substituted[91] anthracene, pyrene and other polyaromatic compounds. Due to the presence of hydroxy groups at the periphery of anthracene derivatives **24** and **25**, supramolecular polymers are formed in the solid state through hydrogen bonding and, hence, favourable conditions for the effective exciton migration are created and the sensor response to the presence of nitroaromatic compounds is enhanced. Thus the material obtained from 9,10-bis(3-hydroxy-3-methylbut-1-ynyl)anthracene (**24**) is able to detect TNT and 2,4-DNT at the nanomolar level (2.0 and 13.7 ppb, respectively). The material based on sensor **25** demonstrates effective photoluminescence quenching (λ_{em}^{max} = 480 nm) in solution in the presence of PA ($K_{SV} = 2.1 \times 10^3$ litre mol^{-1}), while in the solid state, effective photoluminescence quenching (up to 77% in 35 s) occurs in the presence of nitrobenzene vapour.

Structure 24

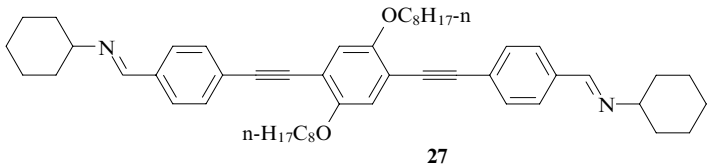


24

Structures 25–27



25, **26**



27

R = $C_6H_3(CO_2H)_2$-3,5 (**25**), Ph (**26**)

In order to enhance the sensing properties of 9,10-bis(phenylethynyl)anthracene (BPEA, **26**), Ponnu and Anslyn[92] prepared a water-soluble cyclodextrin–BPEA complex. In aqueous solutions of TNT and its derivatives, these analytes are encapsulated in the lipophilic cavity of cyclodextrin, and BPEA fluorescence is quenched.

A similar principle underlies the use of a set of organic micelles with dissolved fluorophores such as 9,10-diphenylanthracene, concentrated and dilute solutions of pyrene and the pyrene–perylene FRET system. The method sensitivity depends on the sensor and micelle types, while the detection limit, for example, for TNT can be as low as 19 μmol·litre^{-1} (see Ref. 93).

Chinese authors[94] reported a water-soluble sensor obtained from per-6-amino-β-cyclodextrin with pre-grafted fluorescein molecule [by the reaction with fluorescein 5(6)-isoythiocyanate]. When made to react with TNT in concentrations of down to 20 nmol litre^{-1} in aqueous solutions, this sensor showed FRET quenching of fluorescein photoluminescence *via* the formation of the Meisenheimer complex between the cyclodextrin amino groups and TNT.

A French research team[95] reported a prototype of a portable device for the detection of nitroaromatic compounds in air. The sensing element of the device is based on highly fluorescent diimine **27**. Upon contact of the sensor with air containing down to 6 ppb of TNT and down to 148 ppb of 2,4-DNT, photoluminescence of imine **27** was quenched. According to the authors, the detection has a high degree of selectivity and is not affected by traces of water or aromatic compounds in the air under analysis.[95]

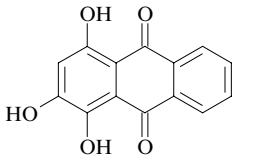
The toxicity of pyrene often hampers its use in bio- and immunosensors (used, for example, to detect nitroaromatic compounds in aqueous solutions). Therefore, Meaney and McGuffin[96] employed sensor matrices based on coumarin, purpurin (**28**), acridine orange, methylene blue, malachite green (**29**), phenol red (**30**) and fluorescein. These dyes have low toxicity and long excited state lifetimes (τ_0 = 1–4 ns). By titration of these sensors with a TNT solution in water, rather high Stern–Volmer constants were obtained (K_{SV} = 50–140 litre mol^{-1}) as compared with pyrene (K_{SV} = 300 litre mol^{-1}). The fluorescence quenching of the sensors is due to the PET process. In the authors' opinion, sensor matrices of this type are applicable for detecting TNT and its derivatives in aqueous solutions.

Highly fluorescent (due to the PET process) 2,2′-disubstituted (*S*)-binaphthyl **31** in solutions, in the solid state and as thin films supported on a glass plate demonstrated fluorescence quenching by 81% in 10 min upon contact with TNT in air and by 54% in the same period of time in the case of 2,4-DNT.[97] The high affinity of chemosensor **31** to nitroaromatic compounds is caused, in the authors' opinion, first of all by the geometry of the molecule. For example, the presence of chiral binaphthyl in molecule **31** accounts for the helical arrangement of the stilbene moieties, which increases the porosity of films of these compounds. Also, the efficiency of detection depends on the type of solvent used to prepare the supramolecular sensing clusters. Indeed, a decrease in the solvent polarity (going from chloroform to toluene) promotes the formation of self-assembled spherical structures due to the dipole–dipole interactions between the molecules of **31**.[97]

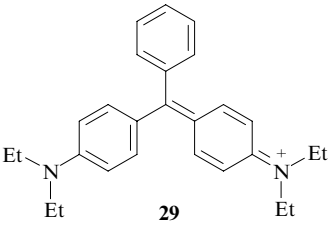
Indian researchers[98] pursuing the goal of fabrication of a molecular chemosensor for fluorescence detection of nitroaromatic compounds synthesized a series of fluoroanthrenes **32**. Owing to the extended annulation system, these molecules can form supramolecular assemblies through π–π interaction between aromatic groups.

Photophysical measurements and quantum chemical calculations demonstrated that by varying substituents at the periphery of fluoroanthrenes **32**, it is possible to change the energy gap between the LUMO and HOMO from 3.44 to 3.88 eV ad thus to affect the chemosensor properties of compounds in solution and in the solid state. Particularly, elongation of the chain of conjugation increases the intensity of the sensor response down to 20 ppb of TNT in the vapour and 1 fg in PA, TNT and

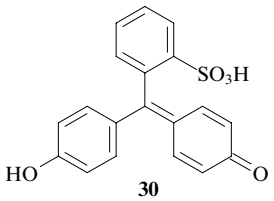
Structures 28–31



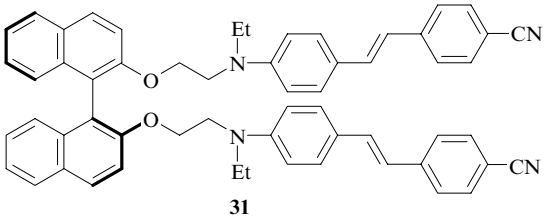
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29



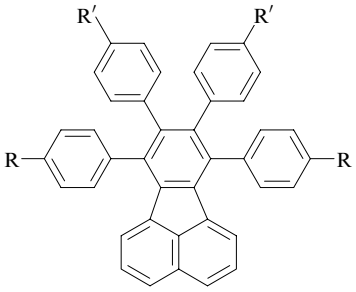
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31

2,4-DNT solutions [$K_{SV} = (1.7-1.9) \times 10^3$ litre mol^{-1}, $\lambda_{em}^{max} = 475$ nm]. In thin films, the sensitivity of fluoroanthrenes to nitroaromatic compound vapours is comparable with the sensitivity of polymeric sensors.

Structures 32



32

R = H, Ph, Bu^n; R′ = H, OC_6H_{13}-n

c. Iptycenes

Due to its unique three-dimensional architecture, namely, a considerable free volume[99] (Fig. 11) and low aggregability, iptycenes have found use as investigation objects in synthetic organic chemistry and material chemistry.[100, 101]

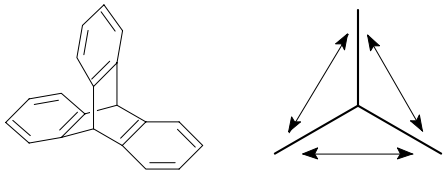
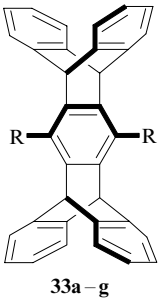


Figure 11. Free volume of iptycene molecule.

In 1998, Yang and Swager[102] published a pioneering study dealing with the use of iptycene chemosensors to detect nitroaromatic explosives. They used the copolymer based on arylacetylenes and 1,4-disubstituted [1.1.1^b.1.1]pentiptycene **33a**. Due to the presence of numerous monomer units, each functioning as a receptor group, the contact with a nitroaromatic compound (electron acceptor) induces fast exciton migration along the polymer chain to the contact site, *i.e.*, the whole polymer behaves as a single molecule. This is a consequence of a uniform electron density distribution along the whole polymer; therefore, the electron is free to move like it moves in electric wires. Swager and co-workers[102–104] interpreted this phenomenon by using the 'molecular wire' notion, which they proposed earlier. This phenomenon ensures the potentially high sensitivity of conjugated polymers to nitroaromatic compounds. In most typical cases, on contact with nitroaromatic explosives, polyiptycene demonstrates almost immediately the intense (> 50%) fluorescence quenching. Gao *et al.*[105] noted that the molar extinction coefficient of these polymers can reach 10^6 litre mol^{-1} cm^{-1}, the electron or energy transfer time being, in most cases, in the femtosecond range. To put it in other way, most of conjugated polymers can be used to detect only nitroaromatic compounds but not other classes of nitro derivatives.

Structures 33



33a–g

R = C≡CH (**a**), benzothiophen-2-yl (**b**), phenyl (**c**), 9,9-bis(2-ethylhexyl)-fluoren-3-yl (**d**), phenylethynyl (**e**), 2,2′-bithiophen-5-yl (**f**), 2-thienyl (**g**)

Using DFT calculations, Swager and co-workers[106, 107] estimated the sensing capability of these polyiptycenes. It was found that if a polyaromatic compound (*e.g.*, triphenylene) is introduced into a conjugated polymer, particularly this moiety is responsible for the formation of a stable π-complex with an electron-withdrawing nitroaromatic molecule (*e.g.*, TNT). When there is no polyaromatic moiety in the polymer, then, according to calculation data,[106] the complex formation with nitroaromatic compounds involves, most likely, the dialkoxyaryl moiety.

These assumptions, however, can be considerably supplemented by the modern results obtained by Swager's (see http://web.mit.edu/tswager/www/Current%20Research-PEMW.htm) and Enlow's groups (see http://sc.tamu.edu/research/cagin/abinitio/study). The DFT (B3LYP 6-31 + G* algorithm) calculations[108] of polyiptycenes demonstrated that molecular complexes (in particular, inclusion complexes) can be formed between nitroaromatic compounds and iptycene moieties (Fig. 12). It was shown that theoretically, the iptycene **33a**–TNT inclusion complex can have both parallel and perpendicular arrangement of the nitroaromatic molecule with respect to the aromatic nuclei that form the iptycene cavity.

The quantum chemical data are consistent with the results obtained by the group of Anzenbacher Jr.[109, 110] They demonstrated for the first time that 1,4-(het)arylpentiptycene derivatives **33b–g** can be used as effective monomolecular photoluminescent chemosensors for nitroaromatic explosives (Fig. 13).

The cavity of these pentiptycenes can accommodate a 2,4,6-trinitrotoluene molecule to reversibly form a donor–acceptor inclusion π-complex. Upon titration of chemosensors **33** in organic solutions in the presence of nitroaromatic compounds, the authors observed intense fluorescence quenching with the constants $K_{SV} = (1.0-5.0) \times 10^3$ litre mol^{-1}.

One more piece of evidence for the formation of crystalline inclusion compounds between nitro explosives and these chemosensors comes from crystallographic measurements. Upon crystallization from competing aromatic solvents, for example, benzene, the 1 : 1 crystalline complex chemosensor **33**–benzene was obtained. In the presence of nitrobenzene, a similar 1 : 1 complex chemosensor **33**–nitrobenzene was formed. In both cases, the face-to-edge orientation of the (nitro)aromatic guest inside the sensor molecule is observed.[111]

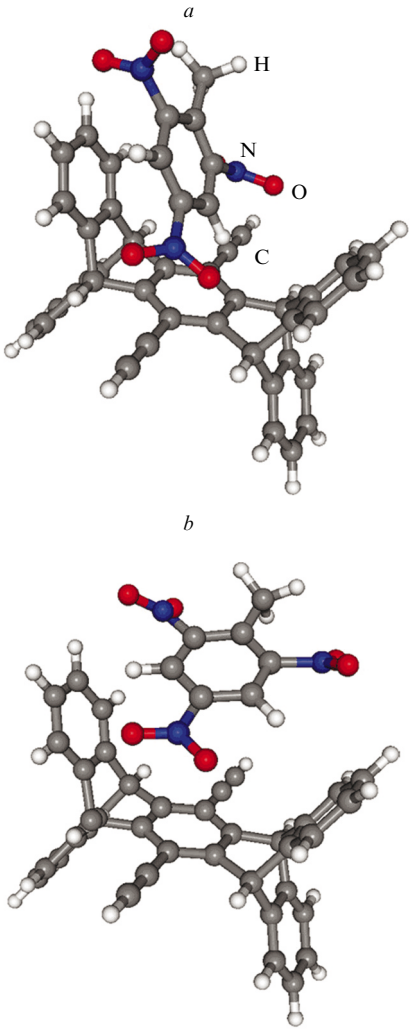


Figure 12. Optimized structures of the inclusion complex of TNT and iptycene moiety **33a** (R = C≡CH) obtained by Autodock (*a*) and RHF6-31G (*b*) algorithms.[108]

At the next phase, the authors manufactured sensing materials to detect vapours of nitroaromatic compounds in air. Having been dissolved in polyurethane matrices and placed on the surface of glass plates (Fig. 14, 15), chemosensors **33b**,**f** showed photoluminescence quenching by 50%–60% with respect to the internal standard in the presence of DNT or TNT vapour with the subsequent complete restoration of the initial values of photoluminescence intensity.

To increase the efficiency of sensing materials by means of the electrospinning procedure, the authors fabricated ultrathin fibres down to 100 nm thick based on the polymers used (see Fig. 14). As a result, in the presence of TNT (10 ppb) and DNT (180 ppb) vapours, photoluminescence of nanofibres is quenched by 30% in 100–120 s and by 80%–90% in 300 s.

As in the cases described above, nanostructuring, first, increases the active mass exchange area and, second, creates conditions for the efficient exciton migration between the chemosensor, the nanofibre and the nitroaromatic compound.

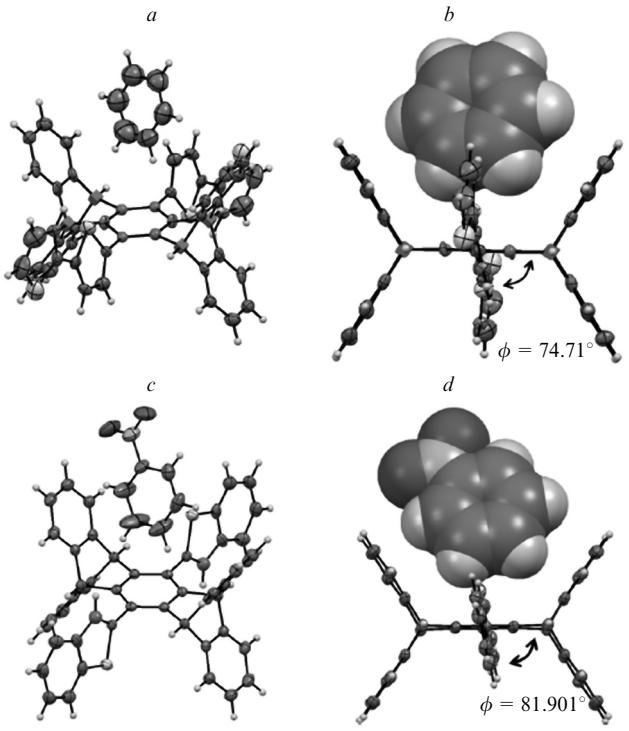
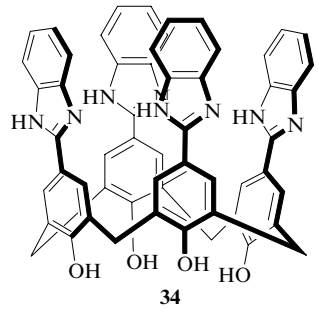
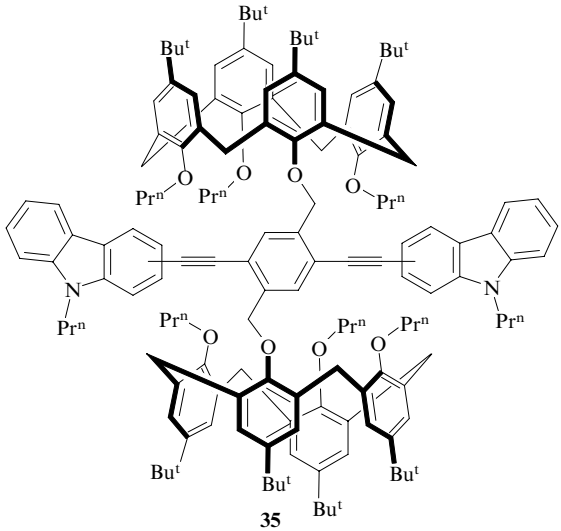


Figure 13. Arrangement of benzene (*a*, *b*) in the pentiptycene **33f** cavity and of nitrobenzene in the pentiptycene **33b** cavity (*c*, *d*) according to X-ray diffraction data: *a* and *c* are top views, *b* and *d* are side views.[109]

Structures 34, 35



34



35

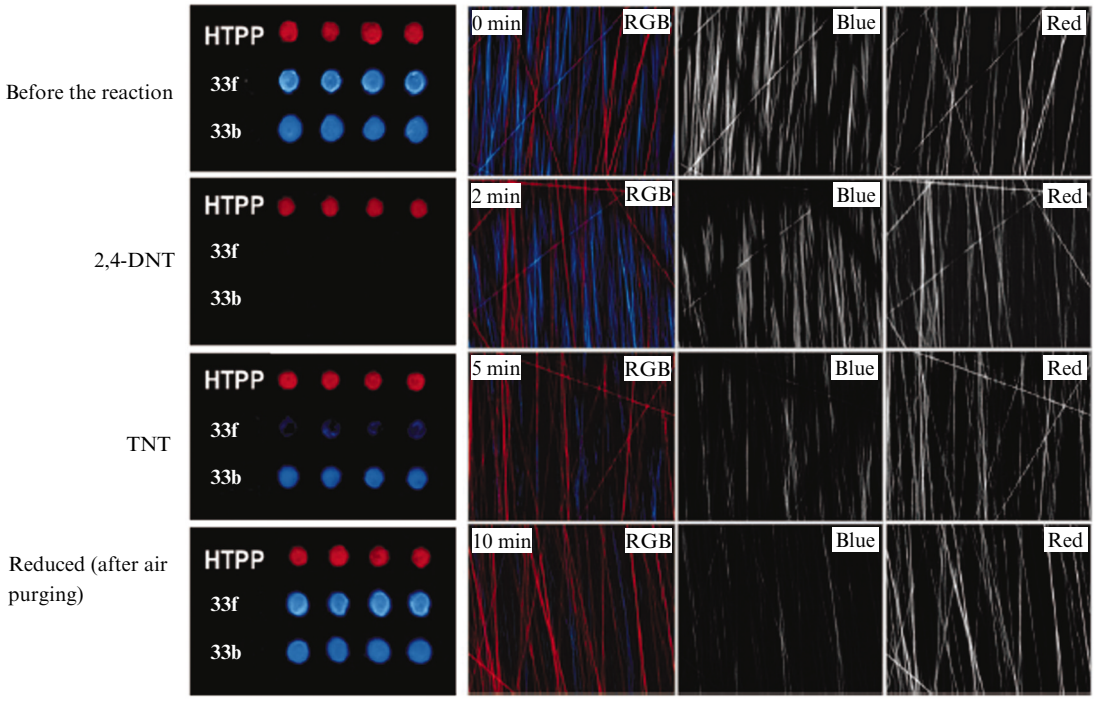


Figure 14. Photoluminescence quenching of nanostructured fibres of pentiptycenes **33** in the presence of TNT vapour with time [tetraphenylporphyrin (HTPP) as the internal standard].[109]

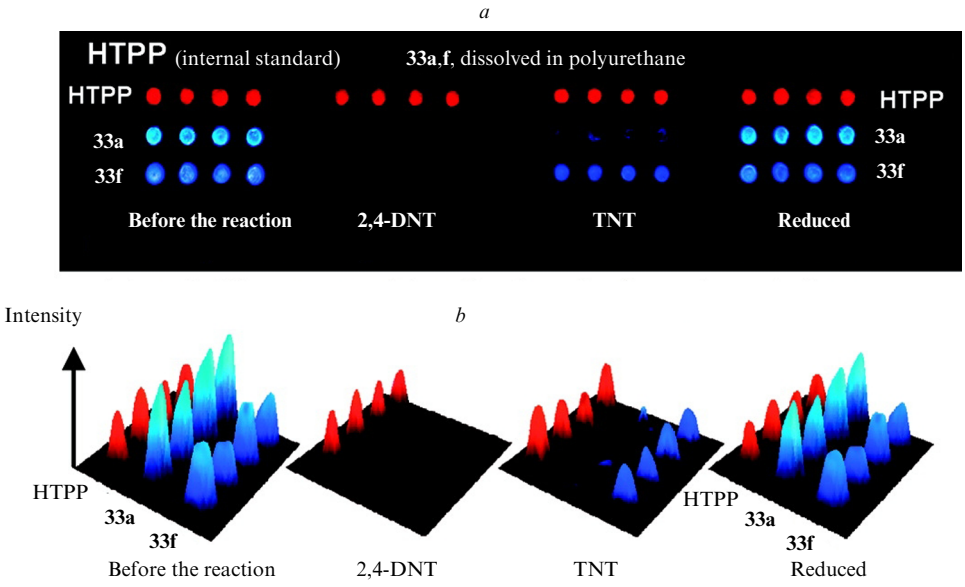


Figure 15. Photoluminescence quenching of polymeric matrices with dissolved pentiptycenes in the presence of TNT and DNT vapour with time (tetraphenylporphyrin HTPP as the internal standard).[110]
(*a*) Photograph of the plate before and after the reaction of DNT and TNT at 22 °C and after reduction in a flow of clean air; (*b*) integrated fluorescence intensity of the fluorophores in the matrix in the quasi-3D-form.

Electron-excessive calix[4]arenes are convenient objects for non-covalent binding (most of all, encapsulation) of electron-deficient analytes, cations of various nature[112–114] including nitrosonium[115,116] and nitronium cations,[117] (poly)nitroaromatic cations[118] and neutral analytes (nitroaromatic[119,120] and polyaromatic compounds[121–123]).

However, only few publications (see, for example, Ref. 124) describe studies aimed at the preparation of effective chemosensors for the detection of nitroaromatic

explosives. First of all, this is due to the lack of effective sensor response to the contact of calixarenes with nitroaromatic analytes, excepts for the development of intense colour upon the formation of CTC with NO_x species resulting from degradation of nitroaromatic compounds.[115–117]

In this connection worthy of note are the publications of Indian[125] and Portuguese[126] researchers concerned with the preparation of photoluminescent sensors based on calix[4]arenes for TNT and its derivatives. The Indian researchers synthesized calixarene **34** functionalized at the upper rim by benzimidazole residues. Unfortunately, quantum chemical calculations demonstrated that calixarene molecule **34** can accommodate up to three TNT molecules in the inner cavity. Therefore, the photoluminescence method proved to be useful for the detection of TNT and its derivatives in solutions but unsuitable for detecting these analytes in air; hence, the authors used the piezoelectric method as the key detection technique.[125]

Barata and Prata[126] synthesized fluorescent sensor **35** based on calix[4]arene modified at the lower rim by 2- and 3-ethynyl-substituted carbazole moieties. Owing to the presence of the calixarene 3D molecule, when deposited on a solid surface, sensor **35** forms a highly porous photoluminescent material demonstrating luminescence quenching by up to 80% in 30 s upon contact with a TNT or 2,4-DNT vapour in air. It is noteworthy that calixarene **35** showed a sensor response to the presence of these analytes comparable to that of polymeric sensors containing polyphenylethynylene-modified calix[4]arenes.[127]

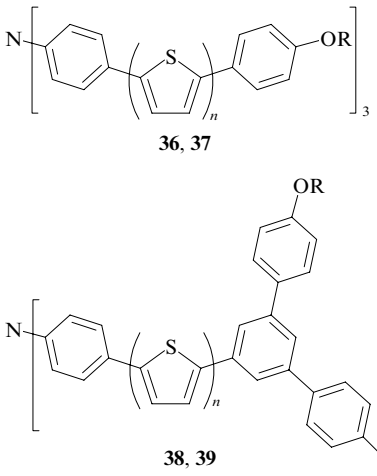
d. Dendrimers and oligomers

Although dendrimers are usually regarded as polymers, most often, they are lacking an efficient system of conjugation of multiple bonds, and, hence, the exciton migration along the system is either limited or absent. In most cases, an effective sensor response in dendrimers is attained *via* generation of several excitons. Oligomers also occupy an intermediate position between monomer molecules and polymers.

In view of the above, chemosensors based on dendrimers behave similarly to small molecules, the most pronounced contribution to the fluorescence quenching being made by collision quenching, which is probably due to steric hindrance to the formation of the chemosensor–nitro compound molecular complex.

For example, Olley *et al.*[128] described a case of collision fluorescence quenching upon the reaction of tridentate dendrimer sensors **36**–**39** (R is 2-ethylhexyl) based on triphenylamine and substituted arylthiophenes. Since for the collision quenching, the nitroaromatic compound (quencher) should diffuse towards the fluorophore during the time of existence of the excited state (upon the contact, the fluorophore returns to the ground state without photon emission), the steric accessibility of the fluorophore is significant. Indeed, the authors observed the highest quenching constants for chemosensor **36**, which is the least sterically hindered but simultaneously it is the weakest electron donor for the formation of a molecular complex (which is the condition for static quenching). Yet another piece of evidence for a large contribution of dynamic quenching is the decrease in the sensor fluorescence lifetime upon photoexcitation as a result of titration

Structures 36–39



36, **37**

38, **39**

n = 1 (**36**, **38**), 2 (**37**, **39**); R is 2-ethylhexyl

with solutions of nitro compounds, indicating that a considerable contribution is made by collision quenching. Furthermore, the titration with solutions of 2,3-dimethyl-2,4-dinitrobutane having a branched structure (hampering the formation of molecular complexes through π–π interactions) entails fluorescence quenching of sensors **36**–**39** (Fig. 16).

An increase in branching (number of the generation) of the dendrimer with the simultaneous formation of several excitons also considerably enhances its sensor response to the presence of nitroaromatic analytes. Guo *et al.*,[129] who used fluorene-based dendrimers **40**–**43** of different generations, observed enhancement of the sensor response to the presence of TNT in solutions ($K_{SV} \leqslant 1400$ litre mol^{-1}) following the increase in the generation number of the dendrimer molecule, namely,

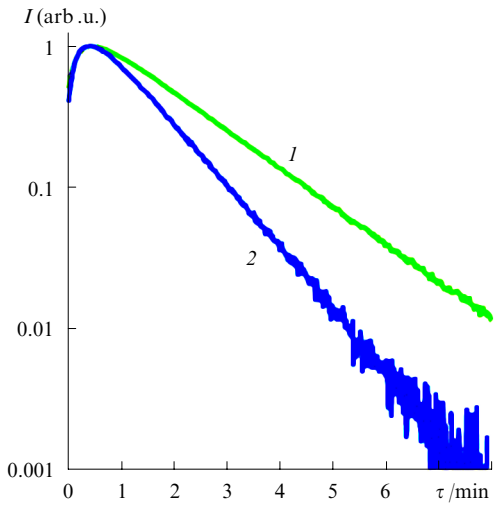
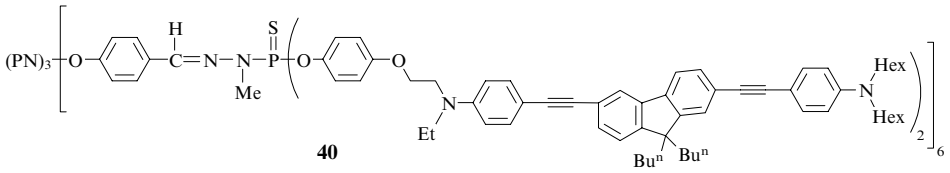
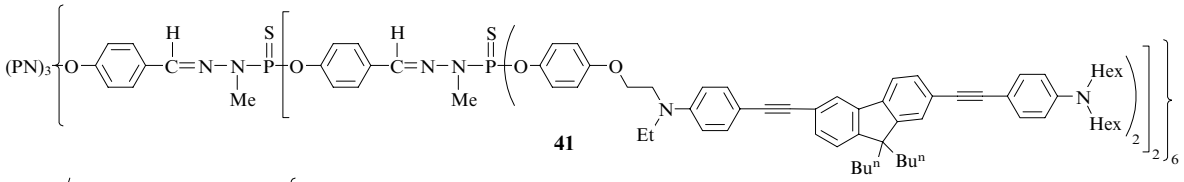


Figure 16. Decrease in the fluorescence lifetime (τ) of sensor **36** in the presence of DNT vapour as an example of dynamic fluorescence quenching.[128]
Fluorescence lifetimes: (*1*) for free sensor **36** , (*2*) in the presence of DNT.

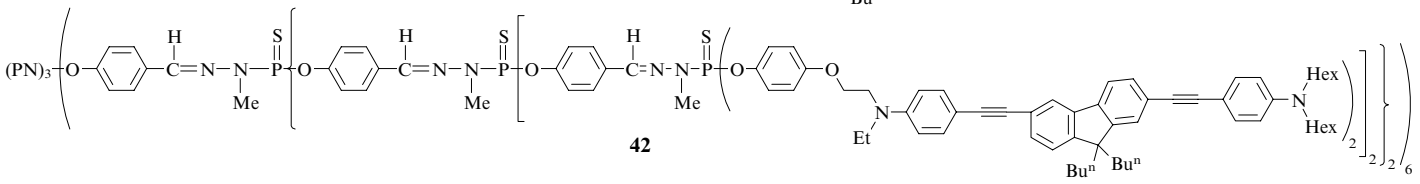
Structures 40 – 45



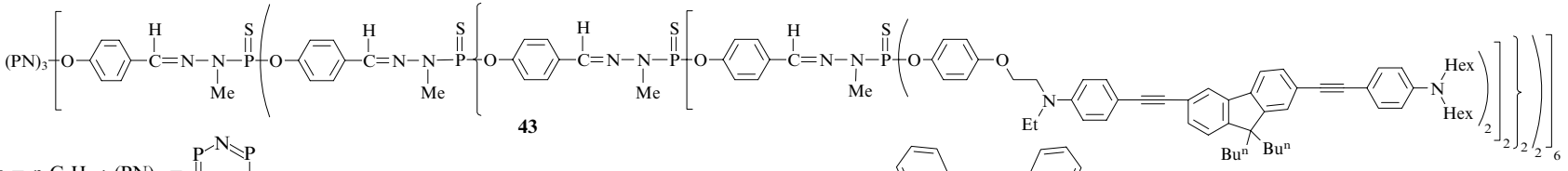
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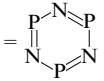
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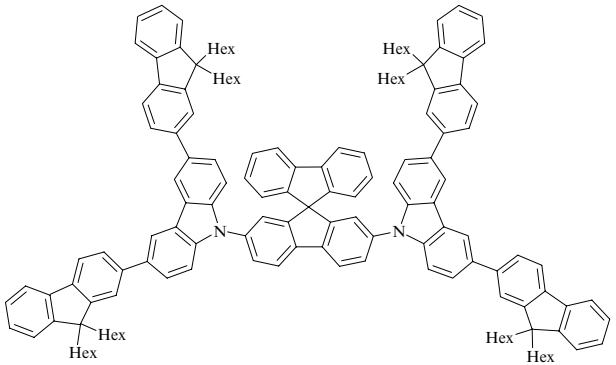


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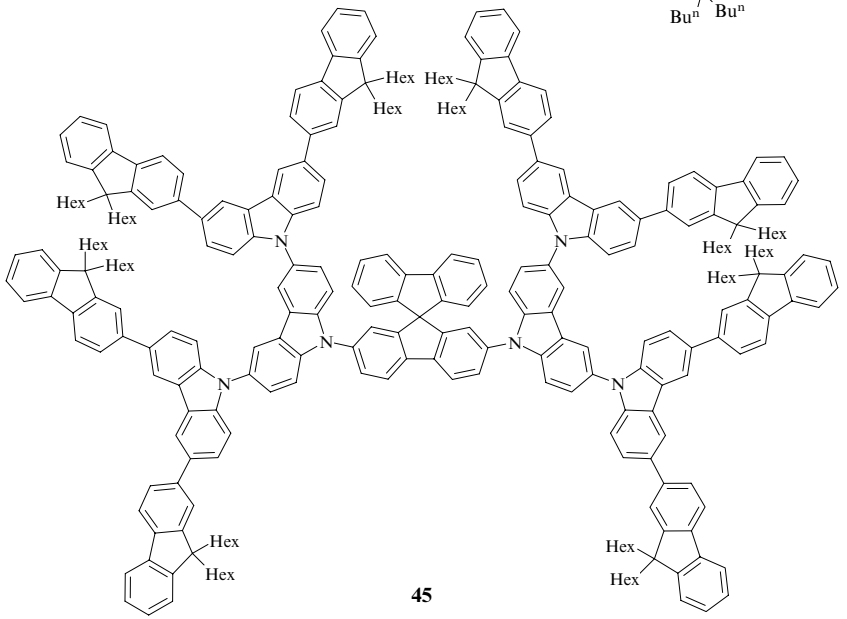


43

Hex = n-C_6H_{13}; $(PN)_3$ = 

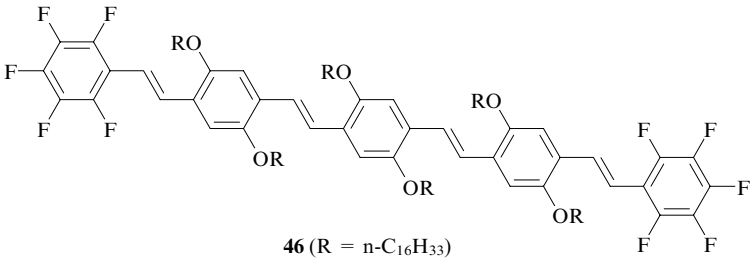


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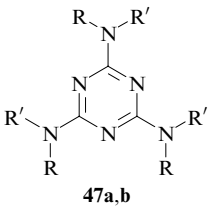


45

Structures 46, 47



46 (R = n-$C_{16}H_{33}$)



47a,b

NRR′ is carbazol-9-yl (**a**), *N*,*N*-diphenylamino (**b**)

on going from **40** to **43**. Measurements of the excited state lifetimes of dendrimer fluorescence attest to simultaneous generation of several excited states.

Carbazole is one more typical component of fluorescent dendrimers for the detection of nitroaromatic explosives, which is due to the ability of carbazoles to form stable molecular complexes with TNT. A group of Australian scientists[130] described carbazole dendrimers — compounds **44** and **45**. The photoluminescent titration of dendrimers in solutions in the presence of nitroaromatic compounds revealed enhancement of the photoluminescence quenching on going from the first generation of dendrimers (**44**) to the second generation (**45**) and then to higher generations; the quenching constants reached 1400 litre mol^{-1}. Solid-state experiments using the films of these dendrimers on glass surface demonstrated that in the presence of nitroaromatic compound vapours, the photoluminescence intensity of the films decreases by 30% during the first 10 s.

In a later publication,[131] the same authors described thin-film sensing materials made of three generations of such dendrimers. All three dendrimer generations were found to successfully detect the nitroaromatic compounds in air by means of reversible photoluminescence quenching. The third generation of dendrimers demonstrates stable, practically irreversible photoluminescence quenching. In the authors' opinion, this is caused by deep penetration of nitroaromatic analytes into the body of the sensing material and its stable retention by strong donor–acceptor interactions.

A Chinese research team[132] obtained a highly porous xerogel, which consisted of nanofibres of carbazole dendrimers formed by π–π-interactions of the (hetero)aromatic moieties. This material detected nitroaromatic explosives in air with a degree of photoluminescence quenching (λ_{em}^{max} = 418 nm) of 77% for TNT and 91% for DNT.

In another work,[133] the authors studied monolayers of *p*-phenylene–ethynylene oligomers, which comprised hydrophilic groups (OH) and hydrophobic moieties (cholesterol) placed on the surface of glass plates. In aqueous solutions in the presence of nitroaromatic analytes, the sensor films containing cholesterol moieties showed the highest sensitivity with respect to PA and TNT. In the authors' opinion, this may be attributed to the lipophilicity of the 'organic layer' formed by cholesterol on the glass surface, which is the driving force of extraction of hydrophobic PA from aqueous solutions.

An unprecedented sensitivity to TNT (10^{-15} mol litre^{-1}) was demonstrated by the photoluminescent xerogel obtained by Indian researchers[134] based on oligo(*p*-phenylene–ethylenes) **46** containing terminal perfluoroaryl groups. The high xerogel sensitivity was attributed to a special packing mode in which the π–π interaction between the electron-deficient perfluoroaryl groups and electron-donating dialkoxyaryl moieties of oligophenylethylene creates favourable conditions for their mutual attraction and for the parallel arrangement of the oligomers relative to one another in the nanofibres, which promotes effective exciton migration.

It is noteworthy that this type of highly ordered arrangement of conjugated and polyannulated aromatic systems caused by complete or partial fluorination of the aromatic ring was observed earlier by other authors.[135–137]

e. Polynuclear heteroaromatic compounds

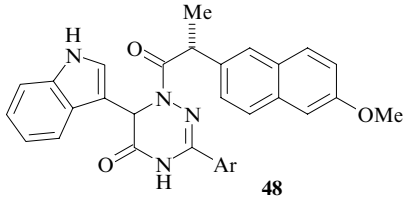
The introduction of a pyridine type nitrogen atom into an aromatic ring, on the one hand, decreases its π-excessive character and the ability to form π-complexes with nitroaromatic compounds. On the other hand, a new heterocycle can serve as a convenient platform for the fabrication of an efficient photoluminscent chemosensor by combining π-excessive receptor and fluorophore moieties into a single molecule and for enhancement of the receptor properties of the molecules by forming π-conjugated donor–acceptor assemblies.

For example, Chinese researchers[138] described a photoluminescence chemosensor for picric acid based on 1,3,5-triazines substituted by 9*H*-carbazole (**47a**) or *N*,*N*-diphenylamine (**47b**) residues. These compounds showed a broad-band fluorescence in solutions and intense narrow-band photoluminescence in the crystalline state with hypsochromic shifts of up to 73 nm. Fluorescent titration of the chemosensors demonstrated intense photoluminescence quenching with Stern–Volmer constants of over 10^7 litre mol^{-1} and detection limits of 15 ppb in the solid state (the chemosensor is aggregated into supramolecular assemblies).

Indian researchers[139] described chemosensors based on quino[2,3-*b*]carbazoles exhibiting photoluminescence in the solid state for the detection of nitroaromatic compounds. These compounds showed intense photoluminescence quenching (λ_{em}^{max} = 385 nm) in solutions in the presence of 2,6-DNT and TNT, which, in the authors' opinion, is a prerequisite for them being used for photoluminescent detection of nitro explosives.

O N Chupakhin and co-workers[140] published data on chemosensors **48** synthesized by direct introduction of indole moieties into 3-aryl-1,2,4-triazin-5(4*H*)-ones in the presence of naproxen. These compounds were used for photoluminescent detection of 2,4-dinitrotoluene and

Structures 48



48

Ar = Ph, 4-MeC$_6$H$_4$

picric acid in solutions. The Stern–Volmer constants obtained from fluorescent titration of chemosensors **48** in the presence of these compounds reached 5×10^4 litre mol^{-1}.

High selectivity of chemosensors **48** to nitroaromatic derivatives might be due to involvement of several types of non-covalent contacts in the complexation, which increases the stability of the chemosensor–nitro compound complex. It is noteworthy that the presence of the indole moiety in molecule **48** is important.

For detection of nitroaromatic compounds in the gas phase using the electrospinning, the authors fabricated nanofibres consisting of polyurethane doped with chemosensors (Fig. 17). These materials demonstrated photoluminescence quenching by 30%–40% in 90–100 s in the presence of 2,4-dinitrotoluene vapour.[141]

The use of indoles as chemosensors for TNT and its derivatives is a result of numerous examples of the formation of stable donor–acceptor complexes between nitroaromatic explosives and indole compounds,[142, 143] including tryptophan metabolites.[144] As regards L-tryptophan, in a recent publication of US researchers,[145] tryptophan showed photoluminescence quenching in solutions in the presence of nitroaromatic compounds with the quenching constants $K_{SV} = (1.7–5.2) \times 10^3$ litre mol^{-1}. Moreover, in aqueous solutions of DMSO, fluorescent proteins comprising tryptophan residues showed a 1.5–2-fold increase in the quenching constants compared with free L-tryptophan, which was attributed by the authors to FRET processes between endogenic tryptophan and protein chromophores. In the presence of TNT and its derivatives, the tryptophan photoluminescence is quenched, inducing the destruction of the FRET pair and quenching of protein photoluminescence. Similarly, in the presence of nitroaromatic compound vapours, the films manufactured from photoluminescent proteins also demonstrated photoluminescence quenching.

According to published data,[146] the photoluminescence quenching efficiency depends on the electron transfer rate from the chemosensor (donor) to the nitroaromatic compound (acceptor); the efficiency of this electronic interaction can be enhanced by introducing Lewis acid fragments (*e.g.*, metals or azinium cations) into the poly(hetero)aromatic sensor.

Aromatic polynitro compounds contain Lewis base fragments (nitro-group oxygen atoms); hence, the interaction with cations or other Lewis acids would accelerate the donor–acceptor electronic interaction and enhance the photoluminescence quenching. For example, Trogler and co-workers[147] demonstrated chemosensors based on polysilols (Lewis bases).

Apparently, monomeric chemosensor based on azatriphenylene developed by O N Chupakhin and co-workers[148] operates according to the same principle. In the presence of nitroaromatic compounds, intensive photoluminescence quenching of the chemosensor takes place. Co-crystallization in the presence of picric acid was found to give stable salts **49** in the solid state.

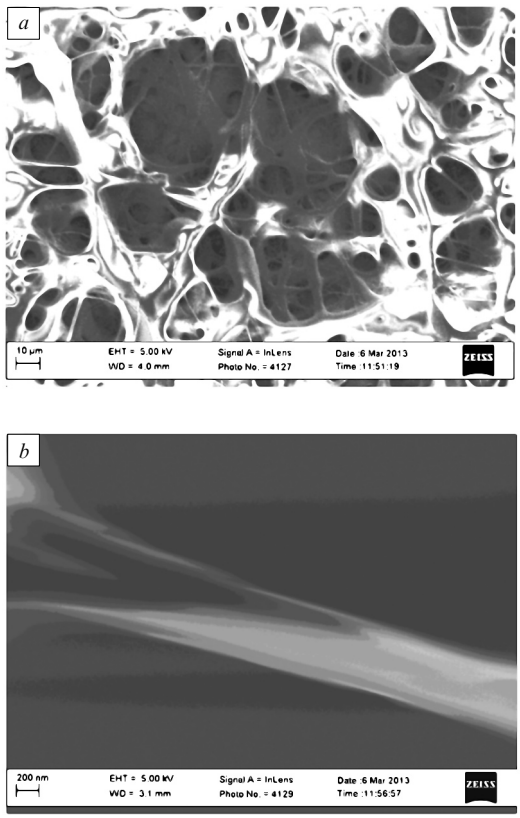
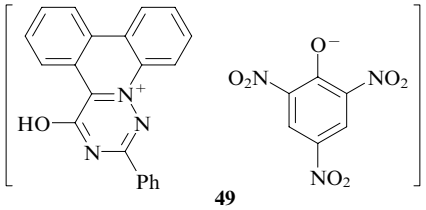


Figure 17. SEM images of the polyurethane nanofibres of chemosensor **48** fabricated by the electrospinning procedure (*a*) and a single fibre (*b*).[141]

The structure of the co-crystallization product of azatriphenylene and PA (salt **49**) was established using the data of X-ray diffraction[149] and elemental analysis.[148]

Indian researchers[150] prepared tris(imidazolium) salts **50a**,**b** for visual detection of TNT and PA. Photoluminescence titration in solutions (λ_{em}^{max} = 399, 422, 446 nm) in the presence of picric acid (detection limit of 352 ppb) demonstrated static fluorescence quenching constants $K_{SV} = (3.3–3.8) \times 10^4$ litre mol^{-1}.

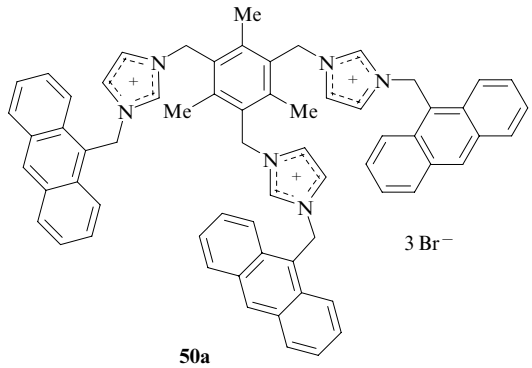
Structure 49



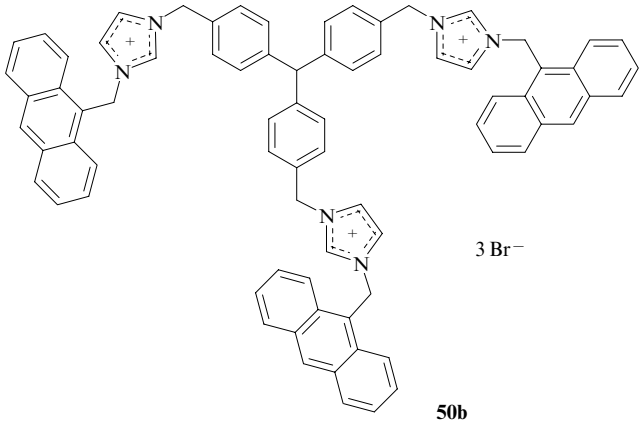
49

The authors believe that the high efficiency of chemosensors **50** for the detection of PA is caused by the possibility of salt formation with the picrate anion

Structures 50



50a



50b

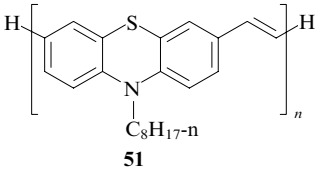
(which was confirmed by X-ray diffraction data for complex [**50a**·2 PA]) and by π–π interactions between the nitroaromatic nucleus of PA and the anthracene moiety. The data of DFT calculations for the ground state demonstrated the possibility of intermolecular charge transfer from PA to compound **50**.

Fluorescent dyes based on xanthene derivatives (for example, 2,3,6,7,12,13,16,17-octahydro-1*H*,5*H*,11*H*,15*H*-diquinolizine-[1,9-*bc*;1′,9′-*hi*]xanthylium salts) introduced into sensor matrices operate in a similar way.[151] In DMF solutions in the presence of TNT and its analogues (for example, TNB), fluorescence quenching takes place, in particular, due to the so-called 'internal filter' effect. The authors assert that the fact that nitroaromatic compounds act as electron donors and the dye molecules are acceptors makes this detection unique.[151]

Liu and co-workers[152] synthesized chemosensors **51** based on oligophenothiazines of different length ($n = 3-5$) for the fluorescent detection of nitroaromatic compounds.

These chemosensors were chosen due to their electron-excessive nature and low reduction potential,[153–155] which is responsible, in the authors' opinion, for their capability of donor–acceptor interaction with nitroaromatic compounds to give molecular complexes. This results in intense PET quenching of green photoluminescence.[152] Fluorescent titration of compounds **51** in solutions in the presence of nitroaromatic compounds demonstrated fluorescence quenching by the static mechanism, as indicated by high quenching constants [$K_{SV} = (4-5) \times 10^3$, $(3.2-3.6) \times 10^3$ and $(3.0-3.5) \times 10^3$ litre mol^{-1} for TNT, DNT and *p*-nitrotoluene (NT), respectively], changes in the absorption spectra of oligomers **51** upon the formation of the molecular complex with nitroaromatic compounds and invariability of fluorescence lifetimes with increase in the concentration of nitro derivatives.

Structures 51



51

$n = 3-5$

Furthermore, owing to the presence of long alkyl fragments, chemosensors **51** proved to be able to form film structures on solid surfaces. These materials are suitable for detecting TNT (detection limit of 4 ppb) and DNT (40 ppb) in air. Other nitroaromatic compounds, including typical organic solvents (*p*-nitrophenol, 2,4-dinitrophenylhydrazine), do not significantly affect the fluorescence quenching of compounds **51**.[156]

For detecting vapours of nitroaromatic compounds, Albert and Walt[157] introduced the photoluminescent dye Nile Red into porous silica gel microspheres (to increase the efficiency of quenching). A sensor matrix of this type was used to detect land-based mines. The sensor matrices were placed on the tip of the visualizing optical fibre and, by means of a charge coupling device, the change in the fluorescence upon contact of the sensors with TNT, 2,4-DNT, 2,6-DNT or 1,3-DNB vapour was detected. The authors note that the sensor response followed a linear dependence on the analyte concentration (1,3-DNB) to an accuracy of 98%.

Chinese researchers[158] described an example of TNT detection in aqueous solutions using fluorescein covalently attached to the surface of amine-functionalized polyethyleneimine (Fig. 18). Upon the TNT contact with free amino groups, the resulting Meisenheimer complex quenches the green fluorescence of fluorescein at 516 nm by the FRET mechanism. In addition, in the presence of TNT, resonance light scattering is observed[159] and also reduces the fluorescein photoluminescence intensity. The researchers cited[158] were able to efficiently detect TNT in solutions in concentrations down to 0.2 nmol litre^{-1}.

An analogous sensor has been described by other researchers.[160] When TNT reacts with amino groups at the periphery of the ethylene–allylamine copolymer, the Meisenheimer complex thus formed quenches the green fluorescence of the covalently grafted fluorescein.

It is known from the literature that solid molecular complexes are formed upon co-crystallization of quinolines with nitroaromatic compounds.[161,162] In a recent work,[163] 2-phenylquinoline was introduced to the periphery of polyacrylates and their copolymers. In the presence of nitroaromatic compound vapours, the authors observed intense photoluminescence quenching of the quinoline moiety ($\lambda_{em}^{max} = 435$ nm); according to the authors, this is a premise for the use of these sensing

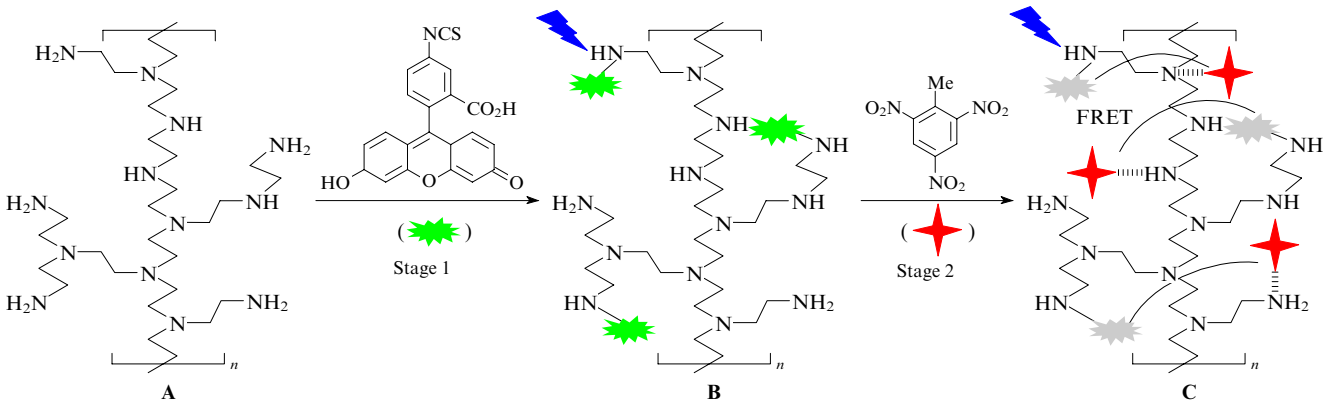


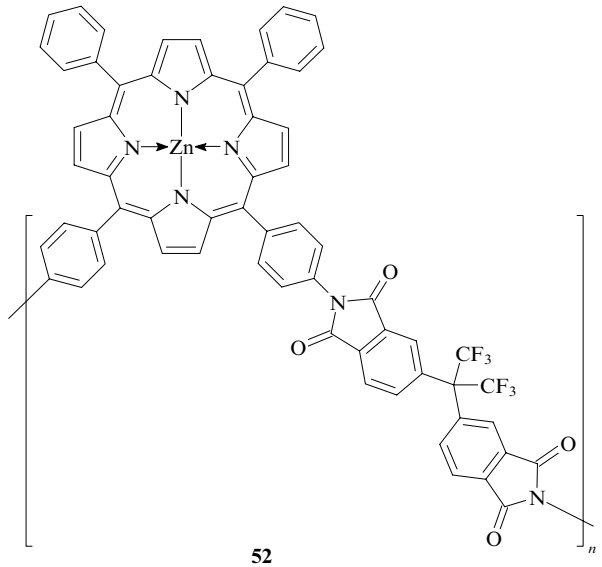
Figure 18. Mechanism of detection of TNT in solutions using polyethyleneimine modified with fluorescein.[158]
A is polyethyleneimine; **B** is fluorescein-modified polymer; **C** is polymer after the reaction with picric acid.

materials for visual detection of TNT and other explosives.

Monomeric porphyrins and zinc porphyrin complexes have a moderate sensing ability with respect to nitroaromatic compounds. For example, in solutions, the quenching constant for these compounds in the presence of TNT reached 0.3×10^3 litre mol^{-1} (Ref. 164). When incorporated in polymer films and nanostructured fibres, tetraphenylporphyrin did not show intense photoluminescence quenching in the presence of vapours of nitroaromatic derivatives.[109, 110]

It was demonstrated [165] that nanostructured polyamide fibres with covalently grafted Zn^{II} porphyrin moieties (structure **52**) are capable of photoluminescent detection of TNT vapour down to 10 ppb concentration [$K_{SV} = (2.37 \pm 0.19) \times 10^7$ litre mol^{-1}], whereas the film of this material was less sensitive to NB, PA, DNT and TNT (the quenching constants were 1–2 orders of magnitude lower). The authors attributed this fact to the presence of self-quenching of porphyrin photoluminescence caused by self-aggregation.[166]

Structure 52



52

f. Coordination compounds of metals with organic ligands

This type of chemosensors combines the advantages of the above-described sensors — intense photoluminescence and photoluminescence quenching in the presence of quenchers. In addition, the introduction of the metal coordination centre into the sensor makes it possible to fabricate chemosensor assemblies of different dimensionality (2D and 3D depending on the metal coordination number) and thus to obtain highly porous materials effective for the detection of various types of energetic compounds.

Yet another advantage of metal coordination compounds with organic ligands is that some metals have their own characteristic emission in the visible region. Some metals, for example, lanthanides (samarium, europium, terbium and dysprosium) exhibit luminescence. Despite the fact that luminescence of simple inorganic salts formed by these ions is weak, it can be substantially enhanced by chelation of the ion by appropriate ligand. The absorption range of the metal complex is determined by the ligand nature, while the emission range is characteristic of each metal ion [167–169] as a result of intramolecular energy transfer from the ligand to the central ion.

The process of this transfer is depicted in Fig. 19 (Figs 19 and 20, see http://www.nanometer.ru/2009/10/27/12565959107489/PROP_FILE_files_7/lumin7.pdf). The organic ligand absorbs energy and transforms from the singlet ground state (S_0) into one of the vibrational sublevels of the first singlet excited state (S_1), where it rapidly loses the excess of vibrational energy. Then two possible scenarios exist involving either relaxation along the $S_1 \rightarrow S_0$ pathway (ligand fluorescence) or transition into a triplet state (T_1). From the triplet state, the molecule can execute spin-forbidden radiative transition to the ground state ($T_1 \rightarrow S_0$) (molecular phosphorescence) or a non-radiative transition.

In addition, intramolecular energy transfer can occur from the triplet excited state of the ligand to the corresponding ^{5}D-energy level (resonance level) of the central metal ion, from which the system can undergo transition to the singlet excited state, which subsequently generates characteristic emission (luminescence) (Fig. 20).

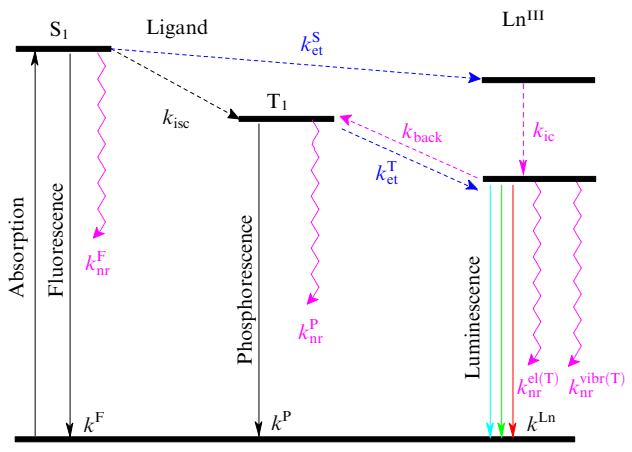


Figure 19. Diagram of the key energy migration paths in coordination compounds [exemplified by lanthanides(III)].
The following designations are used: back is the back energy transfer, e1 is electronic, vibr is vibrational, nr is non-radiative, (T) is temperature-dependent, ic is internal conversion (of electron or energy), isc is the intersystem crossing; et is electron transfer; the superscripts stand for the following: F for fluorescence, P for phosphorescence, Ln for lanthanide ion.

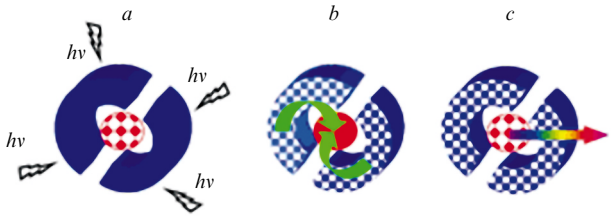


Figure 20. Metal ion luminescence sensitization in coordination compounds [exemplified by lanthanides(III)].
(*a*) Energy absorption by the ligand, (*b*) energy transfer to chelated metal, (*c*) photoluminescence.

There exist two mechanisms accounting for the nature of the triplet–singlet energy transfer from the donor to the acceptor. Dexter (cited by Ref. 170) proposed a mechanism according to which excitons directly migrate between atomic groups, the process efficiency being determined by the nature and the degree of orbital overlap of the interacting systems. Formally, this transition is spin-forbidden; however, this process is possible if the donor exciton decays and is transferred to the acceptor *via* electron exchange. In some cases, this process is considered to be unlikely, because this requires decay of the donor exciton. Förster [171] developed an alternative theory according to which molecular dipoles are connected and transfer energy. In this situation, the efficiency of energy transfer is determined by Eqn (2).

$$\eta_{ET} = \frac{k_{ET}}{k_{ET} + k_r + k_{nr}} = \frac{1}{1 + (r/r_0)^6} \qquad (2)$$

where k_{ET} is the rate constant for energy transfer, k_r and k_{nr} are the rate constants for radiative and non-radiative energy loss by the donor, r is the donor–acceptor distance, r_0 is the distance by which the energy is transferred with a 50% probability.

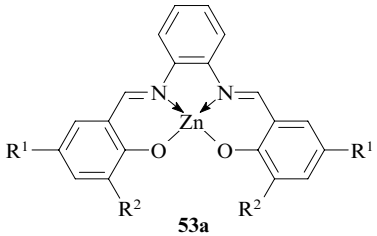
According to this theory, k_{ET} and k_r are proportional to the oscillator strength of the transition. The efficiency of energy transfer almost does not depend on the oscillator strength if $k_r \ll k_{nr}$, *i.e.*, if the donor effectively phosphoresces, the triplet-to-singlet energy transfer mechanism is allowed within the framework of this theory. Förster [172] predicted the presence of these transitions and later this approach was confirmed experimentally.[173] This mechanism explains, in particular, the energy transfer under conditions where the antenna is not directly involved in the chelation of the lanthanide cation.

Thus, advantages of sensors based on coordination compounds include the possibility of selecting the chromophore part of the ligand in such a way that upon contact with a nitroaromatic compound, the $S_0 \rightarrow S_1$ transition energy will change (fluorescence quenching) or transition into one of the triplet states T_1 will be precluded. Additionally, one should take into account the possibility of coordination of nitro-group oxygen atoms, which are weak Lewis bases, to the chelated metal (Lewis acid), which will be accompanied by intense photoluminescence quenching.

Despite the attractiveness of using these chemosensors for the photoluminescent detection of nitro compounds, only few such examples are reported in the literature.

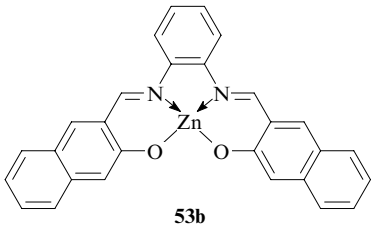
For example, Knapp and co-workers [174, 175] synthesized fluorescent salicylaldimine Zn complexes **53a**,**b**, which show combined static and dynamic fluorescence quenching in solutions in the presence of nitroaromatic compounds (for 2,4-DNT, $K_{SV} = 2-10$ litre mol^{-1}). The authors suggest that in the presence of nitro(aromatic) compounds, weak coordination of the oxygen atoms of the nitro groups (Lewis bases) to the chelated zinc ion occurs in salicylaldimine zinc complexes **53a**, and this is accompanied by fluorescence quenching by the photo-induced charge transfer mechanism. This type of photoluminescence quenching is especially typical of aliphatic nitro compounds unable to form π-complexes with the organic ligand of the metal complex.

Structures 53



53a

$R^1 = R^2 = H$, Bu^t; $R^2 = H$: $R^1 = OMe$, Bu^t, Cl, NO_2



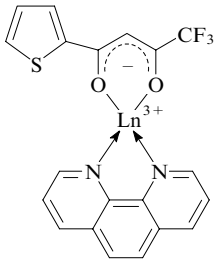
53b

Owing to this unique feature, the above-described chemosensors could be combined into rapid test kits for the detection of nitroaromatic compounds. Each of the nitro derivatives has a characteristic response to the sensor fluorescence. The sequence of readings of each sensor recorded in the presence of nitroaromatic compounds provides the bar graph of sensor responses (readings). Thus, a particular nitro derivative has its own 'fingerprints', which ensure unambiguous identification.[176]

The coordination sensors **54** based on organic chelates of lanthanides operate according to the same principle.[177] In organic solutions in the presence of nitroaromatic and other nitro compounds, the phosphorescence of europium and terbium chelates is quenched due to coordination of the oxygen atoms of the nitro groups to the chelated Eu^{3+} or Tb^{3+} cation. This detection method was used for the first time and proved efficient for identification of 'fingerprints' on the surfaces.[178]

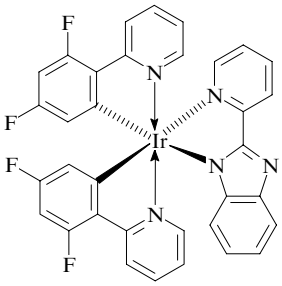
Recently, the research team headed by Reddy and coworkers[179] synthesized the chemosensor based on iridium(III) complex **55**, which demonstrated high ability to detect TNT as vapours, in the solid state or in aqueous solutions by means of photoluminescence quenching.

Structures 54, 55



54

Ln = Tb, Eu



55

In aqueous solutions of organic solvents, the authors observed the formation of highly fluorescent supramolecular structures as a result of chemosensor self-aggregation. This was used to manufacture test strips for rapid detection of nitroaromatic compounds, for example, in drinking water.

g. Luminescent detection of nitroaromatic compounds using micro- and nano-sized materials

Recently, indicator systems based on the use of organic/inorganic matrices (composites or supramolecular assemblies) functionalized on the surface by aliphatic and aromatic amine groups have found the widest use. It is expected that in these sensing materials, the nitroaromatic compound (analyte) would be uniformly distributed between the particular sensing elements and the synergism of the matrix and the sensing element would enhance the affinity of the sensing material for the target object.

For example, Wang and Zou[180] placed 3-aminopropyltriethoxysilane on the surface of manganese-doped (AF MnD) zinc sulfide (ZnS) quantum dots. This material detects TNT in aqueous solutions due to the formation of an intensely coloured Meisenheimer complex of type **1** (see Scheme 1). Simultaneously photoluminescence of the quantum dot is quenched (Fig. 21). The TNT detection limit by this device is 50 nmol litre^{-1}.

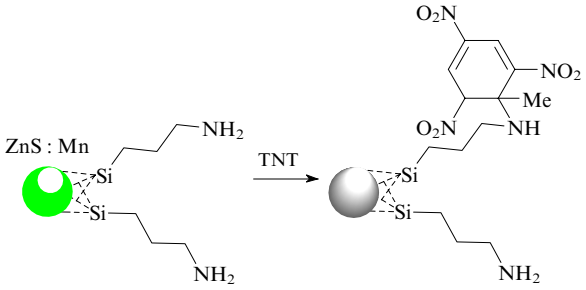


Figure 21. Quenching of the ZnS : Mn quantum dot photoluminescence in the presence of TNT.

In another case, nanoparticles were fabricated from ZnS quantum dots functionalized by terminal amino groups and 8-hydroxyquinoline moieties (also able to form donor–acceptor complexes with TNT and its derivatives[162]) as an additional receptor group and fluorescent marker. The contact with TNT in solution affords the Meisenheimer complex (due to TNT reaction with free amino groups), which intensely quenches (through the FRET process) green photoluminescence of nanoparticles. The decrease in the photoluminescence intensity follows a linear dependence on the TNT concentration with a TNT detection limit of 10 nmol litre^{-1}.[181, 182]

A sensor without quantum dots, simpler in application, was fabricated[183] by deposition, on a paper surface, of nanospheres obtained by the reaction of Al 8-hydroxyquinoline complex with organic polymers (*e.g.*, polyurethane). In aqueous solutions in the presence of down to 32 ng ml^{-1} of TNT, the authors observed quenching of the green photoluminescence of the Al complex.

Israeli researchers[184] prepared nanosensors consisting of CdSe/ZnS quantum dots modified by strong electron-donating groups — polyphenols and aniline. In the presence of TNT, PA and other analytes, intense photoluminescence quenching of the quantum dot (from 20% to 70%) was observed in solutions of these nanosensors. The efficiency of the donor–acceptor interaction depended on the nature of the nitroaromatic explosive and/or the type of substituent at the periphery of the quantum dot [for example, for picric acid $K_{SV} = (4-9)\ 10^3$ litre mol^{-1}].

Spanish authors[185] fabricated photoluminescent CdSe/ZnS quantum dots doped with creatinine (2-amino-1-methyl-5*H*-imidazol-4-one) moieties to be used for photoluminescent detection of TNT and its derivatives. Upon their contact with nitro explosives, selective quenching of quantum dot photoluminescence is observed. In the authors' opinion, high selectivity of detection of nitroaromatic compounds (for TNT, 10 μg litre^{-1} in water and down to 0.057 μg g^{-1} in soil) is determined by the Jaffe reaction,[186, 187] which is widely used in clinical medicine for quantitative determination of creatinine (as the muscle metabolism product) in biological fluids.[188]

The cheapest and most easy to manufacture sensing material was obtained by the reaction of 1,6-hexamethylenediamine-functionalized magnetic Fe_3O_4 nanoparticles

with fluorescein (as a fluorescein label).[189] According to the results obtained by the authors, the contact of these nanoparticles with TNT results in the adsorption of the TNT anion on the surface of an amino-functionalized nanoparticle and intense photoluminescence quenching of the fluorescein moiety at 519 nm. The material shows a high selectivity with respect to TNT, the quantification limit being 37.2 nmol litre^{-1}.

As described above, some metal salts possess their own photoluminescence, which may be used for the fabrication of metal-organic frameworks (MOF) to detect nitroaromatic analytes. For example, a benefit of lanthanide-containing MOF is the intense narrow-band photoluminescence, which allows these MOF to be used for the design of various photoluminescent materials and devices.[190, 191]

Using a surfactant (trimethylcetylammonium bromide) and the reaction of benzene-1,3-dicarboxylic acid (BDA) and $EuCl_3 \cdot 6H_2O$, Ding *et al.*[192] prepared nanocrystalline clusters $[Eu_2(BDA)_3(H_2O)_2]_n$ with a diameter of 100–200 nm and a length of 10–30 μm. Having been dispersed in acetonitrile, these nanocrystals demonstrated photoluminescence quenching (λ_{em}^{max} = 595 and 616 nm) in the presence of *o*- and *m*-nitrotoluenes or 2,6- and 2,4-DNT.

Ma and Wang[193] observed quenching of the green photoluminescence (λ_{em}^{max} = 543 nm) of nanoparticles obtained by the reaction of the inorganic complex $NaYF_4:Yb^{3+}/Er^{3+}$ with 3-aminopropoxytriethylsilane (forming the Meisenheimer complex on contact with TNT) and ethylene glycol dimethylacrylate. This material is suitable for detecting 9.7 ng ml^{-1} of TNT in solutions even in the presence of competing analytes such as PA, DNT and NB.

Previously the same research team[194] manufactured supramolecular nanocomposites (nanospheres) consisting of the magnetic component Fe_3O_4, the photoluminescent component $LaF_3:Ce^{3+}(Tb^{3+})$ and the binder — an oleylamide and succinimide copolymer. Upon contact with a mixture of nitroaromatic analytes, the reaction of the $C(O)NH_2$ receptor group with TNT results in the formation of a stable donor–acceptor complex, which causes irreversible photoluminescence quenching at λ_{em}^{max} = 545 nm, whereas in the presence of other nitroaromatic compounds, the nanocomposite photoluminescence can be restored by means of magnetic separation (Fig. 22). According to authors' data, other nitroaromatic compounds, including PA, did not have a significant effect on the photoluminescent detection of TNT by the above-described nanocomposites.

Yet another group of researchers utilized nanostructured silica gel modified by aliphatic amine groups (responsible for the formation of the Meisenheimer complexes in the reactions with TNT and its derivatives) and residues of fluorescent dyes — 5(6)-carboxyfluorescein-*N*-hydroxysuccinimide (so-called C1609 dye)[195] or 6-carboxyrhodamine.[196] The dye was so selected that its fluorescence was substantially quenched *via* FRET upon the formation of the Meisenheimer complex between TNT and amine (Fig. 23).

More recently, chemosensor **56** based on nanostructured silica gel modified by aliphatic amine groups was developed.[197] As the signalling group, this sensor contained nitrobenzoxadiazole (nitrobenzofurazan), which is

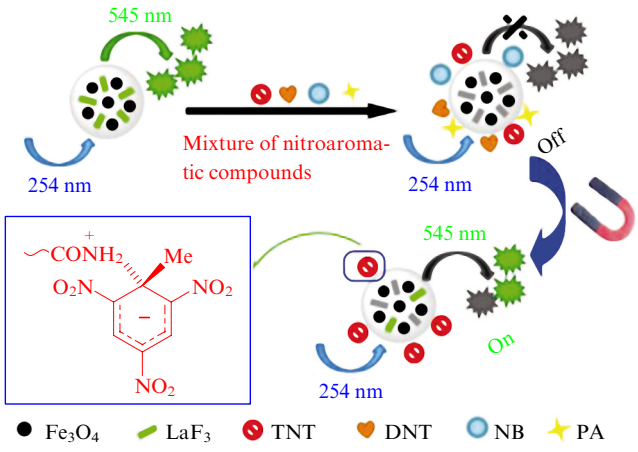
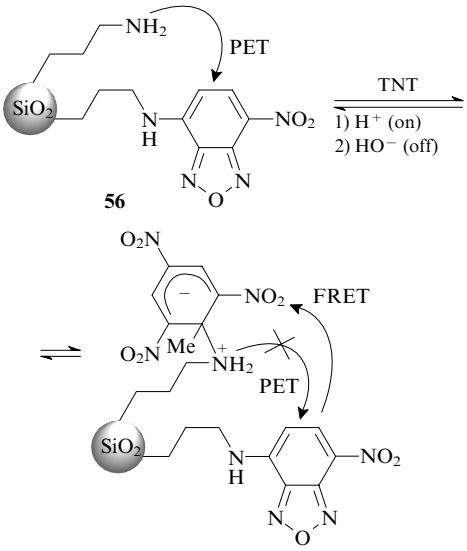


Figure 22. Interaction of photoluminescent nanocomposites with TNT and other analytes.[194]

Scheme 9



a rather widely used fluorophore for the detection of various analytes, including TNT (Scheme 9).

The sensitivity of sensor **56** depends on the ratio of the nitrobenzofurazan moieties and free amino groups: when

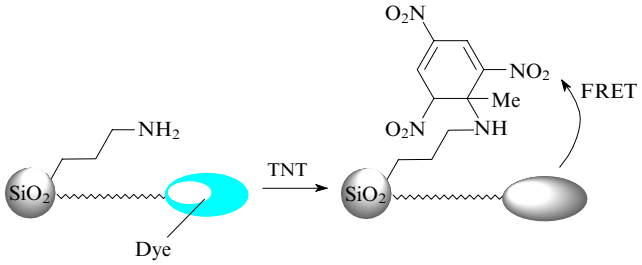


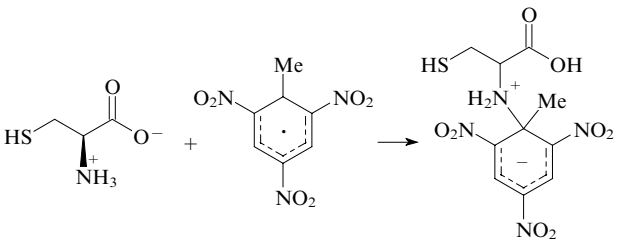
Figure 23. Photoluminescence quenching of nanostructured silica gel modified by aliphatic amino group and dye moieties in the presence of TNT and its derivatives.

this ratio is 1 : 40, the photoluminescence quenching in the presence of TNT is most pronounced.[198] The authors believe that on the silica gel nanoparticle surface, the nitrogen atoms of free amino groups partially quench photoluminescence of nitrobenzofurazan by the PET mechanism. In the presence of TNT, the PET process is inhibited by the formation of the Meisenheimer complex, which quenches the nitrobenzofurazan photoluminescence by the FRET mechanism. The protonation of amino groups, even in the presence of TNT, also suppresses the PET process and after alkalization, sensor **56** returns to the initial state.

In another case,[199] nano-sized silica gel functionalized by aminopropyl groups and doped by the $[Ru(phen)_3]^{2+}$ complexes (phen is 1,10-phenanthroline) as a photo- and electroluminescent label was used. In organic solvents in the presence of TNT in down to 0.3 nmol litre^{-1} concentration, this nanocomposite demonstrated an effective sensor response (< 1 min).

Cysteine is known for its ability to react with TNT and its derivatives in solutions to give intensely coloured Meisenheimer complexes [200–202] (Scheme 10, Fig. 24).

Scheme 10



In addition, it can form a covalent bond with TNT even in the gas phase.[203] US researchers [201] used cysteine deposited on the surface of nano-sized gold particles to detect TNT in the gas phase in down to 2 pmol litre^{-1} concentrations. This was accompanied by aggregation of

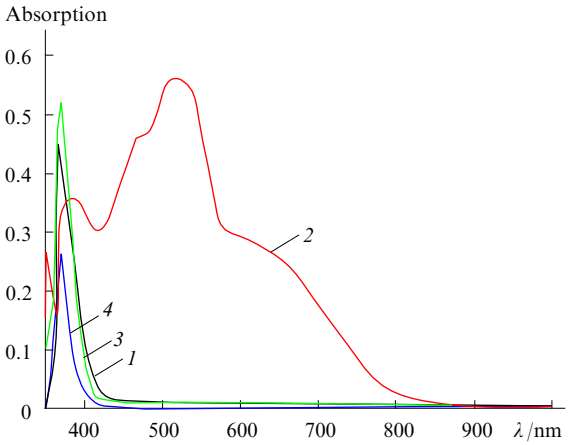


Figure 24. Absorption spectra of solutions: (*1*) TNT, (*2*) cysteine + TNT, (*3*) cysteine + DNT, (*4*) cysteine + nitrophenol.[201]

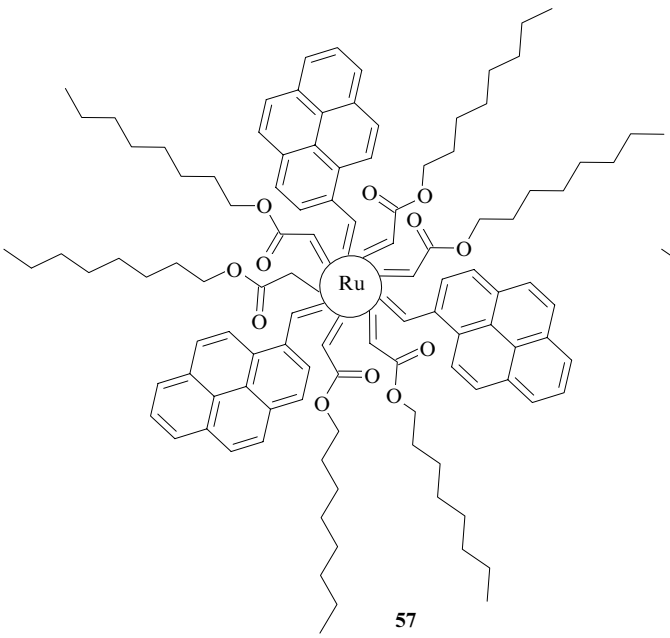
nanoparticles, which can be observed by Raman spectroscopy (surface enhanced Raman scattering, giant Raman scattering).

Cysteamine was used to design an efficient device for visual detection of nitroaromatic compounds.[204] Upon deposition of 3-sulfanylpropionic acid (SPA)-modified quantum dots (QD) CdSe-CdTe on the surface of gold rods functionalized by cysteamine, complete fluorescence quenching took place *via* the formation of the quantum dot–nanorod FRET pairs (Fig. 25).

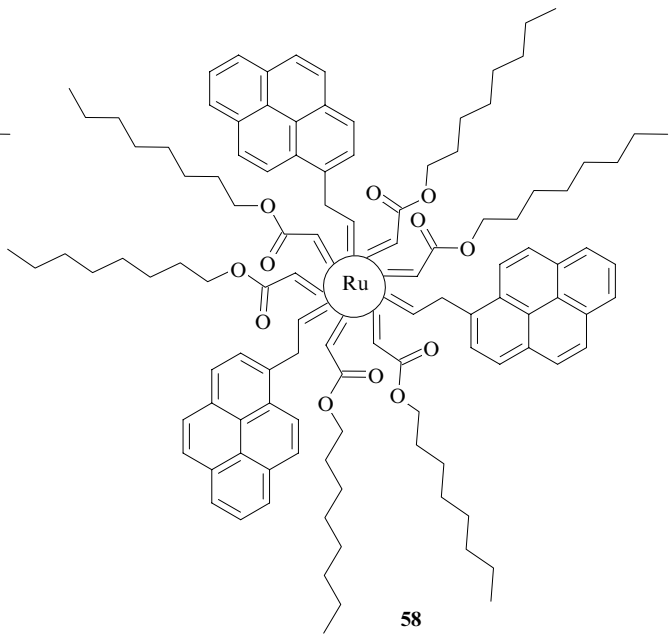
Upon contact with the TNT vapour, the FRET pair was destroyed to give the Meisenheimer complex between the amino group attached to the nanorod and TNT. This was accompanied by fluorescence enhancement. The detection limit of TNT was 0.1 nmol litre^{-1}.

As described above,[78] pyrene and its derivatives are used for direct and indirect detection of nitroaromatic compounds in air and in solutions. However, the pyrene tendency to form poorly soluble excimers limits is use as an individual sensing material. For optimization of the

Structures 57, 58



57



58

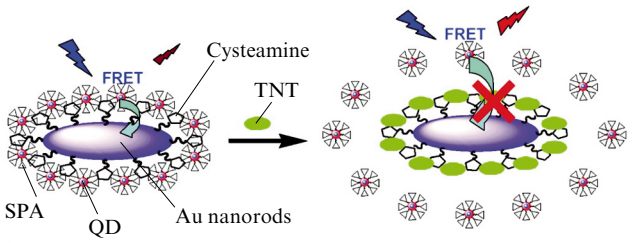


Figure 25. Destruction of the FRET pair of the hybrid nanosensor in the presence of TNT vapour.[204]

sensor response of pyrene, 1-vinyl- and 1-allylpyrenes were prepared and attached to the surface of ruthenium nanoparticles. The obtained nanoparticles **57** and **58** in the presence of nitroaromatic compounds in solutions demonstrated photoluminescence quenching by the dynamic mechanism.

The dynamic quenching mechanism is evidenced by a change in the photoluminescence lifetime. As the length of the carbon linker increases (on going from vinyl to the allyl group), the efficiency of photoluminescence quenching decreases (the quenching constants decrease). The higher quenching constant for nanoparticles with 1-vinylpyrene moieties was attributed to the formation of a supramolecular conjugated structure in which the formation of shorter metal–π-system bonds enhances the energy/charge transfer to the nitroaromatic compound and thus intensifies quenching. A benefit of ruthenium nanoparticles as compared with monomeric pyrenes is that the larger number of chromophores placed on the surface of the ruthenium nanoparticle increases the probability of collision interactions. This results in higher quenching constants [up to $(1-2)\times10^4$ litre mol^{-1} *versus* $(0.2-5)\ 10^3$ litre mol^{-1} for monomeric pyrenes] (Fig. 26).[78]

A US research team [205] described a considerable (up to threefold) increase in the intensity of photoluminescence of rhodamine 6G, which was applied on the surface of nanostructured silicon coated by silver and polymeric dielectric material (organic polymer) nanoparticles. In the gas phase in the presence of TNT, the material demonstrated a 60% quenching of rhodamine photoluminescence (λ_{em}^{max} = 598 nm) in 100 s.

Indian researchers [206] obtained pioneering nanostructured photoluminescent sensors that are actively switched on in the presence of TNT. Curcumin [(1*E*,6*E*)-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-1,6-diene-3,5-dione] was used as the base for these sensors. In the presence of TNT in aqueous solutions, nanoaggregation of curcumin took place accompanied by a 800-fold enhancement of photoluminescence. The authors called this phenomenon the nanomaterial surface energy transfer (NSET).

h. Luminescent detection of nitroaromatic compounds using micro- and nano-sized porous materials

The use of micro- and nano-sized porous materials as matrices for small molecules substantially increases the efficiency of detection of nitroaromatic compounds due to an increase in the active mass exchange surface between the sensor and the analyte. Weak intermolecular interactions of the polymeric matrix with the nitro compound may serve as an additional driving force for transport of

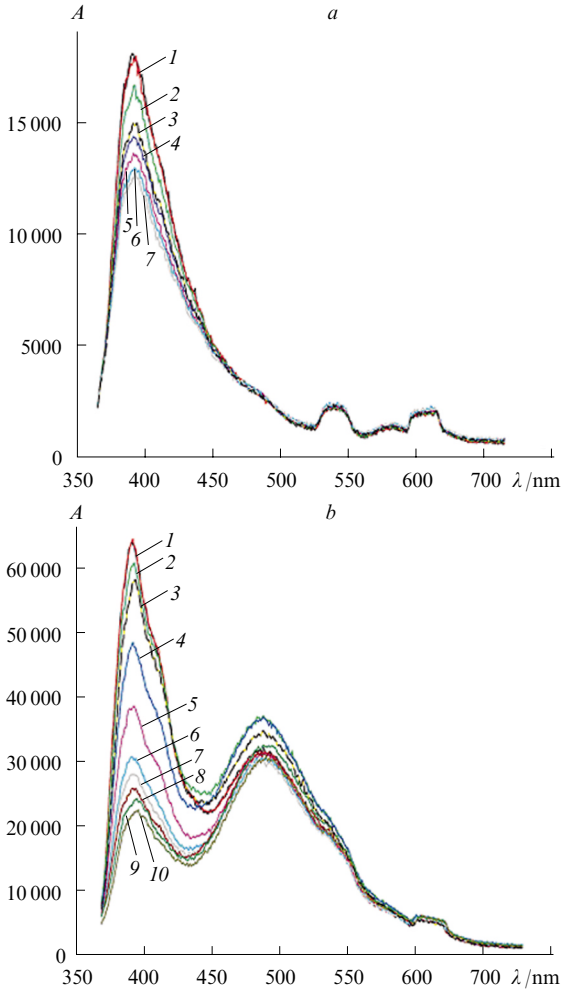


Figure 26. Photoluminescence quenching of ruthenium nanoparticles **57** (*a*) and **58** (*b*) in the presence of nitroaromatic compounds.[78]
Concentration /10^5 mol litre^{-1}: (*a*): 0 (*1*), 0.5 (*2*), 1.0 (*3*), 1.5 (*4*), 2.0 (*5*), 2.5 (*6*), 3.0 (*7*); (*b*): 0 (*1*), 0.002 (*2*), 0.05 (*3*), 0.2 (*4*), 0.5 (*5*), 1.0 (*6*), 1.5 (*7*), 2.0 (*8*), 2.5 (*9*), 3.0 (*10*).

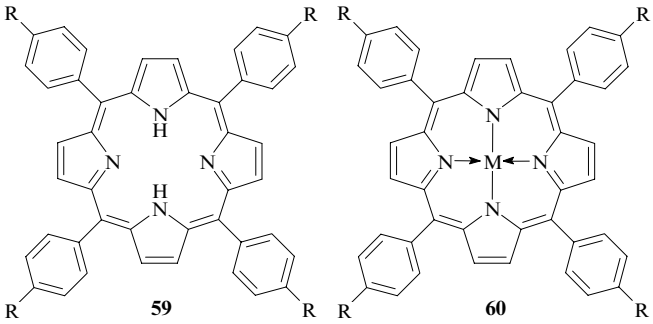
the analyte inside the sensing material, thus ensuring effective complexation with the chemosensor. As a result, effective quenching of the sensor fluorescence takes place by analogy with the sensing materials based on conjugated polymers. In addition, the commensurability of the pores of the polymer matrix and the geometric parameters of the analyte (*e.g.*, TNT) provide an additional sign for its presence even as a mixture with other compounds.

An example of using micro- and nanoporous materials as chemosensors for the photoluminescent detection of TNT and its derivatives is mesoporous silica gel doped with metal porphyrins **59** and **60** reported by Tao *et al.*[207–209] In this case, the synergism of the photoluminescent sensor (porphyrin) and inorganic polymer with a 'smart' solid-phase morphology gives a perfect sensor.

In their first publication,[207] the researchers described the material based on a randomly structured nanocomposite formed by silica gel doped with porphyrin **59**. This material demonstrated high sensitivity to TNT and its derivatives in air: photoluminescence quenching was up to 97% in 120 s. Thus, according to the authors, the nano-

composite they obtained was at least twice more sensitive than other known materials.

Structures 59, 60



59 **60**

R = CO_2H, $C(O)NH(CH_2)_3Si(OEt)_3$; M = Zn^{II}, Cd^{II}

Proceeding from the fact that the morphology and the structure of the inorganic matrix are crucial factors for the design of an efficient sensing material, the same researchers [208] fabricated three types of inorganic silicon polymers, one amorphous, one having a 3D hexagonal (porous) structure and one having a 3D tubular structure (depending on the preparation procedure). As expected, the material sensitivity depended directly on its porosity (mass exchange surface area): in the presence of TNT vapour, a 27% fluorescence quenching of porphyrin placed in the 3D tubular polymer occurred as soon as in 10 s.

Tao *et al.*[209] reported fluorescence quenching of cadmium(II)- (by 60%) and zinc(II)-containing (by 43%) porphyrins and the free porphyrin ligand (by 33%) placed in a 3D tubular mesoporous silicon polymer upon the contact with TNT vapour in 10 s.

Intense fluorescence quenching was observed within several minutes in a 96-well plate on the surface of periodically ordered mesoporous silica gel doped with porphyrin **59** (R = CO_2H) in the presence of TNT in aqueous solutions.[210] According to the authors, the mesoporous silica gel structure ensures its enhanced absorption capacity with respect to TNT (80%–92% of TNT absorption from an aqueous solution) and efficient TNT delivery to the sensing component (porphyrin).

Another Chinese research team [211] manufactured mesoporous hybrid organosilicon polymer films of different morphology and geometric dimensions by modification of block copolymers by silylated naphthol residues. In the most illustrative example, on contact with TNT vapour, the photoluminescence of the film is quenched by up to 96.3% in 1200 s. The same authors reported [212] the preparation of a highly porous polymeric organosilicon material with a peculiar two-dimensional hexagonal structure. Owing to this structure, on contact with TNT, the material photoluminescence is already quenched by 72% in 60 s (due to photoluminescence quenching of silylated naphthol on contact with TNT).

Zhu *et al.*[213] synthesized a series of chemosensors based on ionic liquids, quaternary phenanthro[9,10-*d*]imidazolium salts, placed on the silica gel surface to give mesoporous structures. It was shown that by varying the anion (Cl^-, I^-, PF_6^-, NO_3^-, alaninate, glutamate and Tf_2N^-, where Tf is the trifluoromethanesulfonate) in the quaternary imidazolium salt, one can affect the efficiency of detection of nitroaromatic analytes.

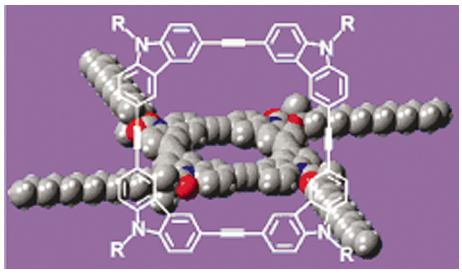
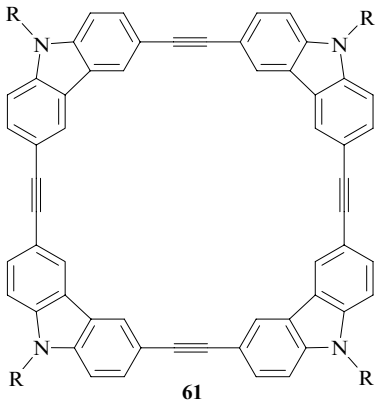


Figure 27. Structure of carbazole tetramer **61**.[214]

Nanofibres obtained from tetrameric carbazole derivative **61** (R = $CO_2CMe_2C_{12}H_{25}$-n) (Fig. 27) exhibit a high degree of fluorescence quenching intensity in the presence of TNT (by 83%) and DNT (by 90%) in air within 60 s.[214]

The high sensitivity of sensing material **61** to less volatile TNT can be due to the highly ordered structure, which ensures high porosity. The electrostatic interactions between the electron-excessive molecules of chemosensor **61** and electron-deficient molecules of TNT and its derivatives provide the effective transport of nitroaromatic molecules inside the material,[214] while the π–π interaction between the (hetero)aromatic chemosensor moieties provides favourable conditions for the intermolecular exciton migration (by the Förster mechanism).[215–217]

Structure 61



61

R = $CO_2CMe_2C_{12}H_{25}$-n

Microporous metal-organic frameworks (MMOF) have also found wide use for the detection of energetic compounds.[218,219] For example, 4,4′,4″-tris[ethynyl-*trans*-$Pt(PEt_3)_2(NO_3)$]triphenylamine reacts with 1,3-di(3-pyridyl)isophthalamide to form supramolecular structure **62** effective for photoluminescent detection of nitroaromatic compounds in solutions.[220] According to authors' data, owing to the specific geometry, six fluorescent acetylene ligands of platinum form a cavity complementary in the size to nitro-substituted benzenes and PA. The intermolecular donor–acceptor interaction results in fluorescence quenching of several molecules that form the supramolecular assembly of chemosensor **62**, similarly to how this occurs in polymers. The Stern–Volmer constants (2×10^4 and 5×10^4 litre mol^{-1} for TNT and PA, respectively)

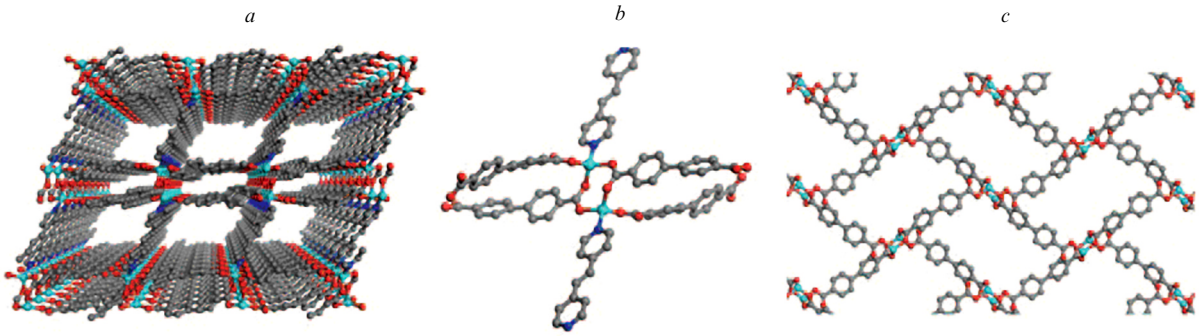
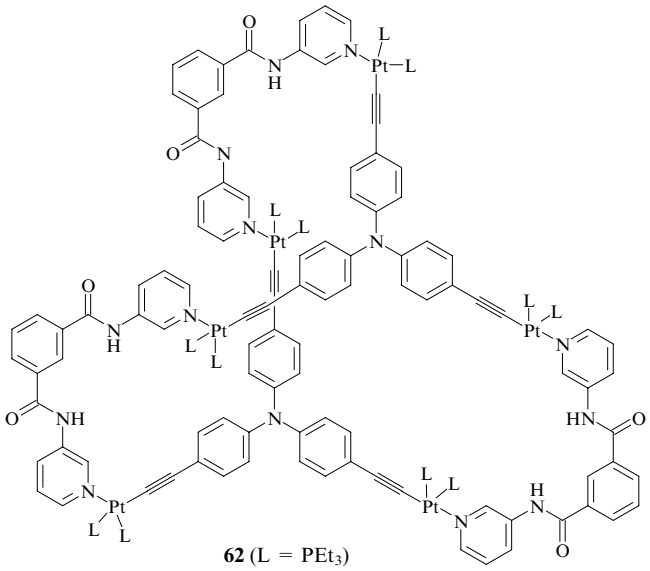


Figure 28. Supramolecular architecture of the complex $[Zn_2(bpdc)_2(bpee)]$ according to X-ray diffraction data.[221]
(*a*) Crystal structure, (*b*) general view of one molecule, (*c*) fragment of one layer.

approach those for polymeric organic or metal-containing sensors.

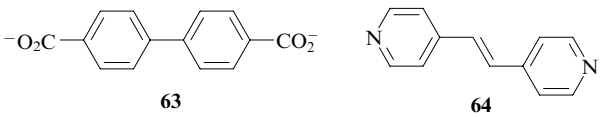
Structure 62



62 (L = PEt_3)

Similarly, the complex $[Zn_2(bpdc)_2(bpee)]$ [bpdc is biphenyl-4,4′-dicarboxylate (**63**); bpee is 1,2-di(4-pyridyl)-ethylene (**64**)] reported by Li and co-workers[221] forms a microporous supramolecular architecture (Fig. 28) capable of effective encapsulation and visual detection of 2,4-DNT in air (*via* photoluminescence quenching).

Structures 63, 64

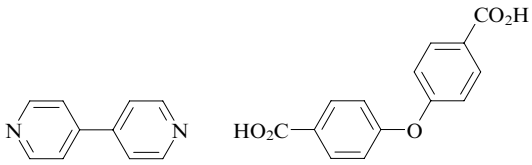


63 **64**

The authors deem that large active mass exchange surface area in combination with excellent photoluminescence characteristics of the material is favourable for detection of both aromatic and aliphatic nitro compounds, in particular, 2,3-dimethyl-2,3-dinitrobutane.

Subsequently, the preparation of one more photoluminescent porous material — $[Zn_2(oba)_2(bipy)]\cdot DMA$ — based on the Zn-complex of 4,4′-bipyridine (bipy, **65**), 4,4′-oxobis(benzoic acid) (oba, **66**) and *N*,*N*′-dimethylacetamide (DMA) was reported.[222]

Structures 65, 66



65 **66**

In the presence of vapours of nitroaromatic compounds (nitrobenzene and 2,4-DNT), intense photoluminescence quenching of the material took place, the quenching rate being directly proportional to the volatility of the nitroaromatic compound (Fig. 29).[222, 223]

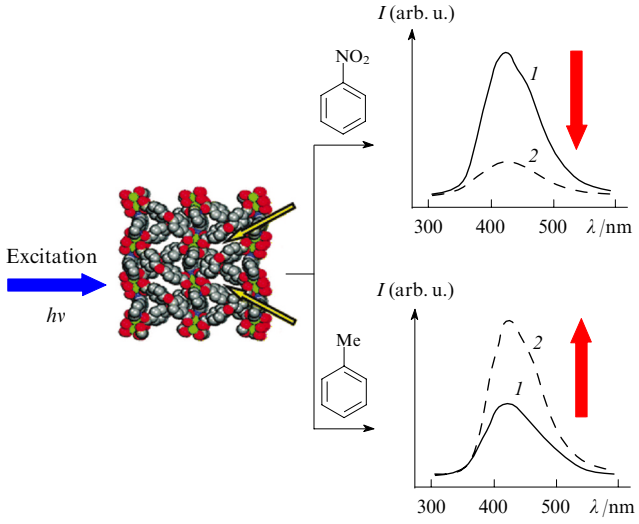


Figure 29. Structure of the $[Zn_2(oba)_2(bipy)]\cdot DMA$ complex and the change in its fluorescence in the presence of a toluene and nitrobenzene vapour.[222]
Curve *1* is emission intensity before the addition of analyte vapour, curve *2* is that after the addition. In the case of toluene, the fluorescence intensity increases (enhancement), while in the case of NB, it decreases (quenching).

Indian authors[224] investigated the photoluminescent supramolecular structure obtained by the reaction of zinc acetate with the π-conjugated ligand — 5-(4-carboxyphenylethynyl)isophthalic acid. During titration in organic solvents (ethanol), the addition of TNT in concentrations down to several ppb results in PET quenching of up to 90% of the material photoluminescence. Hence, this sensor can be used to detect 2,4-DNT and TNT in potable water.

The same authors[225] prepared ternary supramolecular assemblies by the reaction of zinc acetate with 3-arylmethoxyisophthalic acid [Ar = Ph (MOF-1), α-naphthyl (MOF-2), pyren-1-yl (MOF-3)] and 1,4-di(4-pyridyl)benzene. As the supramolecular structure is formed, the aromatic substituents present in the isophthalic acid molecule are directed inside the appearing pores (Fig. 30). Having been dispersed in ethanol, these materials demonstrate sharp photoluminescence quenching (λ_{em}^{max} = 415, 420, 480 nm) in the presence of nitroaromatic compounds. An increase in the size of the aryl substituent decreases the quenching efficiency by decreasing the steric accessibility for explosives on going from MOF-1 to MOF-3. Nevertheless, all of the obtained assemblies showed reversible photoluminescence quenching during several cycles at TNT concentrations down to several ppb.

Chinese authors[226] prepared the nanoporous 3D supramolecular structure $[Cd(ATP)(H_2O)_2]_n$ by the reaction of $Cd(NO_3)$ with sodium 2-aminoterephthalate (H_2-ATP). The photoluminescence of this complex (λ_{em}^{max} = 435 nm) caused by intramolecular ligand–metal charge transfer[227] considerably decreased in the presence of nitroaromatic compounds (nitrobenzene and nitrotoluene) in ethanol solutions, whereas in the presence of other aromatic compounds it remained invariable.[228] In the authors' opinion, this is a consequence of the donor–acceptor interaction between the aromatic ligand and the nitroaromatic analyte, which may subsequently be used for photoluminescent detection of nitroaromatic explosives.[228] Another research group[229] synthesized photoluminescent metal-organic nanotubes with the composition $[Cd_2(BTA)_2(H_2O)_2]$ (BTA is benzene-1,3,5-tricarboxylic acid) with the smallest diameter of 30 nm. In the presence of 2,4-DNT vapour, photoluminescence of nanotubes is quenched (λ_{em}^{max} = 406 nm) by 72.5% in 10 s. The detection limit of DNT (calculated by the procedure proposed in another work[230]) was 18.1 ppb.

Photoluminescent sensing materials for the detection of nitro explosives based on mesoporous silica gel with covalently grafted chromophores (pyrene, fluorescein, dansyl) were reported.[231] In organic solvents, these materials showed efficient photoluminescence quenching in the presence of tetryl and PA with the quenching constants of $(1.0-1.4)\times10^3$ litre mol^{-1} (8.5 to 14.4 ppm) and 1.4×10^4 litre mol^{-1} (1.2 to 1.4 ppm), respectively, and photoluminescence quenching in the presence of tetryl-containing soil samples. The authors attributed the high efficiency of the material to the π–π interaction between the electron-excessive fluorophore molecules and electron-deficient nitro explosive molecules (Fig. 31).

An unusual type of sensor response, namely, photoluminescence enhancement in the presence of TNT and tetryl, was demonstrated by another mesoporous material reported by Salinas *et al.*[232, 233] According to the obtained data, the detection mechanism is based on the fact that on contact with nitroaromatic analyte molecules, the tetrathiafulvalene (TTF) molecule changes its orientation on the silica gel surface *via* the formation of CTC with nitroaromatic compounds (Fig. 32) and liberates the dye $Ru(2,2'\text{-bipy})_3^{2+}$ molecule encapsulated inside the silica gel.

The same researchers[234] described a fluorogenic mesoporous material for the detection of nitroaromatic explosives comprising silica gel with the encapsulated photoluminescent dye $Ru(2,2'\text{-bipy})_3^{2+}$ and pyrene residues grafted to the silica gel surface. On contact with the nitroaromatic compound, the molecular complex pyrene–nitroaromatic compound is formed (quenching of pyrene photoluminescence at 380–430 nm is simultaneously observed) and, as in the case described above, $Ru(2,2'\text{-bipy})_3^{2+}$ is liberated, which is accompanied by enhancement of the photoluminescence with the maximum at λ_{em}^{max} = 625 nm (λ_{excit} = 453 nm) (Fig. 33).

Arylboronic acids are known to contain some amount of cyclotrimerization products, cyclotriboroxanes.[235] Australian and Chinese researchers used this feature to prepare a 3D porous luminescent material based on tetrakis[4-(dihydroxyboryl)phenyl]germanium. This organometallic composite, first, has a large active mass

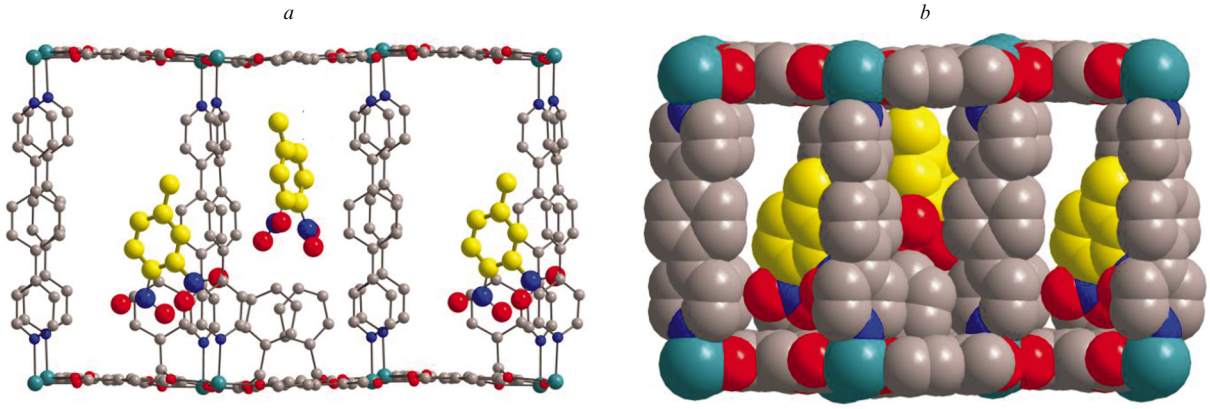


Figure 30. Arrangement of 3,4-DNT molecules inside MOF-1 according to X-ray diffraction data (*a*) and the representation by Stewart–Brigleb 3D models (*b*).[225]

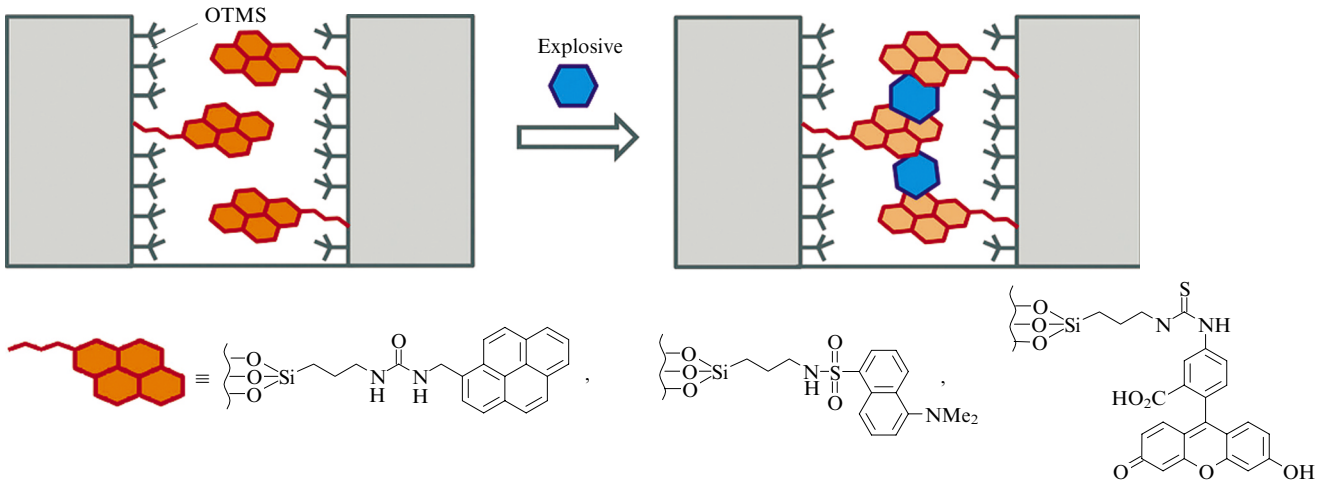


Figure 31. Reaction of nitroaromatic explosive molecules with fluorophore molecules within sensing materials.[231]

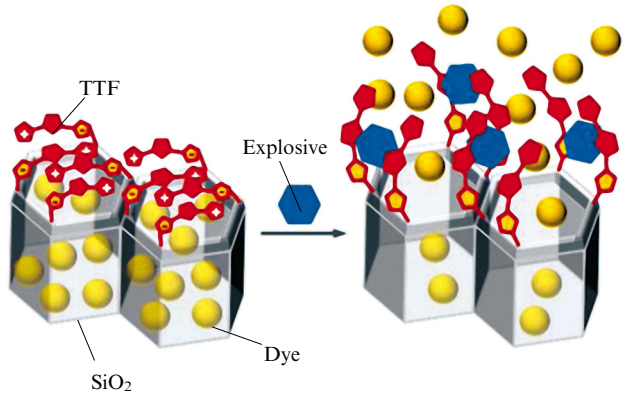


Figure 32. Mechanism of detection of TNT and tetryl by the procedure from Ref. 232.

exchange specific surface area (determined by the Brunauer–Emmet–Teller method[236]), equal to 1288 $m^2\ g^{-1}$; second, it has a small energy gap as its LUMO has low energy (this favours effective electron transfer and formation of a stable non-fluorescent complex with nitroaromatic compounds); finally, third, it provides conditions for effective exciton migration. In the presence of 1.5 to 150 ppm of nitroaromatic compounds (TNT, DNT and NB), this material showed noticeable photoluminescence quenching (λ_{em}^{max} = 371 nm).[237]

III. Electrochemical detection methods

1. Electrochemical (electrical) detection

The electrochemical methods for the detection of explosives are based on the processes on the electrode surface or in the near-electrode space and measurement of the electrical system parameter, which is functionally related to the solution composition and concentration (specific properties), *i.e.*, it is proportional to the quantity of the analyte in the solution. These methods are cheapest, fastest and most convenient, because they do not require expensive equipment. The last two decades have witnessed the development of electrochemical methods for the direct rapid on-site detection of nitroaromatic compounds and

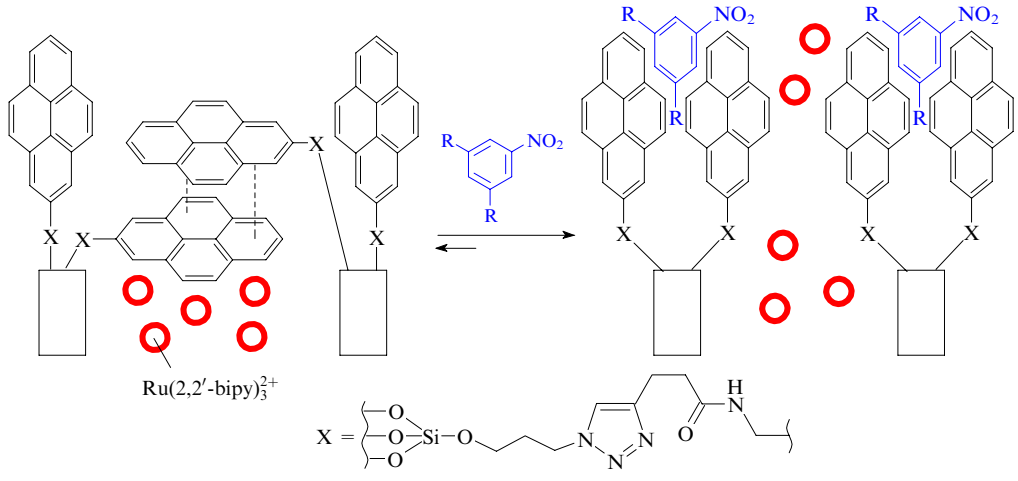


Figure 33. Mechanism of detection of TNT and tetryl by the data of Ref. 234.

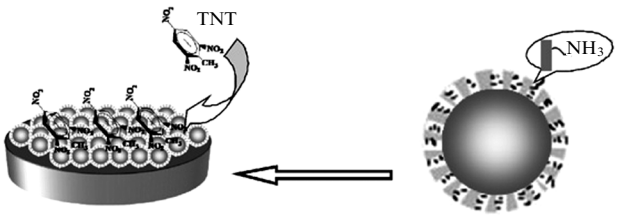


Figure 34. Functionalization of the surface of a carbon electrode by mesoporous silica gel modified with 3-aminopropyltriethoxysilane.[239]

complex analysis of explosive mixtures ('laboratory-on-chip'). The major advantage of electrochemical methods is the possibility to perform measurements in solutions of aqueous and non-aqueous electrolytes. Furthermore, the electrochemical sensors and sensing materials can be pre-modified either chemically or mechanically to enhance their sensor response to the presence of TNT and its derivatives in aqueous and non-aqueous media.[238]

In electrochemical methods, carbon electrodes are used most often, which are modified mechanically or chemically in order to impart higher affinity for nitroaromatic compounds to them. For example, the surface of a carbon electrode is coated by mesoporous silica gel (SiO_2–$mSiO_2$) modified by 3-aminopropyltriethoxysilane to create conditions for a chemical reaction (through the formation of the Meisenheimer complex) with TNT (Fig. 34).[239] Voltammetric measurements showed high efficiency of this electrode for TNT detection (the sensor response is 0.011 μA nM^{-1} higher than that for other nitroaromatic compounds: DNT or 1,3,5-trinitrobenzene). High selectivity to TNT is caused by the large contact surface and by the possibility of TNT preconcentration on the electrode surface due to the more effective chemical reaction with the amino groups (*via* the Meisenheimer complex formation).

The electrode obtained from the nanocomposite of graphene and carbon nanotubes functionalized by ethylenediamine residues operates in a similar way.[240] Upon contact with TNT, the Meisenheimer complex is formed and the electrochemical sensor response appears. According to authors' data, the sensitivity of this electrode to TNT in solutions reaches 0.01 ppb.

The electrostatic and geometric complementarity of the TNT and triphenylene molecules forms the ground for many photoluminescence sensors for nitroaromatic compounds, which have been described in the previous sections of the review. Also, electrodes modified by carbon nanotubes demonstrated a clear-cut sensor response to TNT.[241] Zhang *et al.*[242] combined these two sensor moieties to fabricate a combined electrode modified by both carbon nanotubes and triphenylene residues deposited on the nanotube surface. The electrode obtained in this way showed fast sensor response and enhanced selectivity and sensitivity to TNT compared to conventional carbon nanotubes, which was manifested as a change in the electrode fluorescence and electrical characteristics in the presence of TNT vapour.

2. Micro- and nanoelectrical (electronic) detection

These methods for detecting TNT and its analogues are highly promising for commercialization, as the detection occurs at the micro- and nanomolecular levels and often at the single-molecule level. Therefore, ultracompact sensor devices with low limits of detection of nitro compounds hold a key position among nanosensors (see *2009 NCTC Report on Terrorism, National Counterterrorism Centre*; http://www.nctc.gov/witsbanner/docs).

For example, the nanoelectrical sensor designed by Professor Patolsky's team (Israel)[243] based on nano-sized field effect transistor principle is a real alternative to sniffer dogs (Fig. 35). The device base — a semiconductor silicon nanowire — was coated by receptor groups containing 3-aminopropyltriethoxysilane groups. Upon the chemical reaction of the primary amino groups of the aliphatic part of the amine with TNT (to give the Meisenheimer complex), the change in the charge distribution on the nanowire surface changes the electric field strength, which in turn affects the measured electrical conductivity of nanowires.

Researchers from the USA and Korea[244] used the same principle in the recently designed 'smart' biometric nano-sized device where the sensing base is tripeptide receptor **67** consisting of the tryptophan–histidine–tryptophan amino acid sequence.

The vesicles formed by polydiacetylene and tripeptide **67** were placed on the surface of single-walled carbon

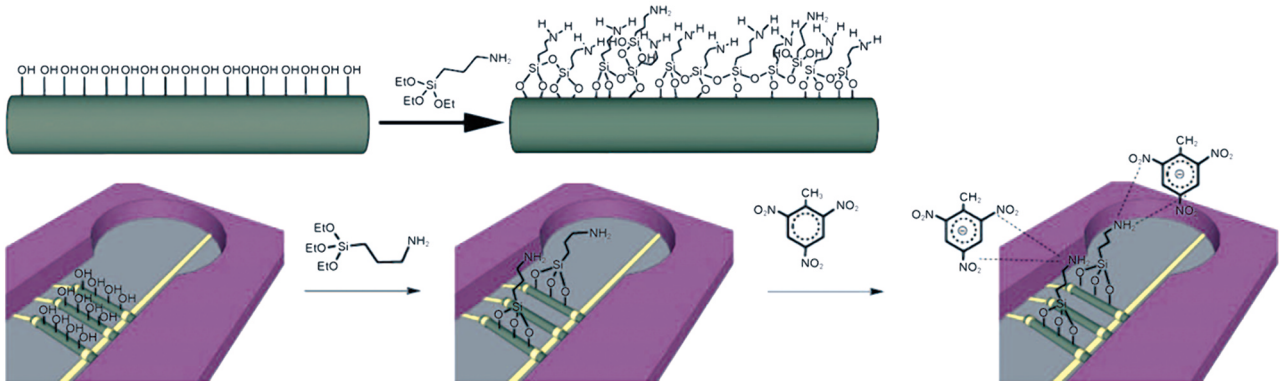


Figure 35. Scheme of 'electronic sniffer dog' for the detection of TNT: the primary amine receptor groups are placed on silicon nanowires.[243]

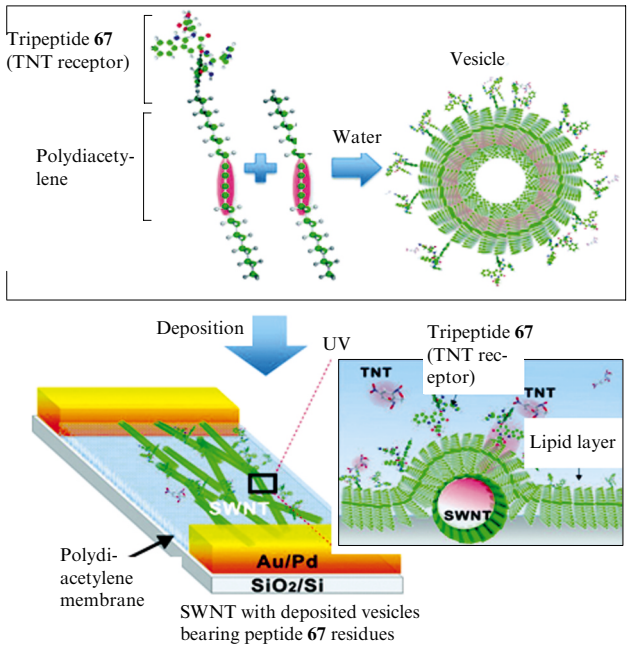
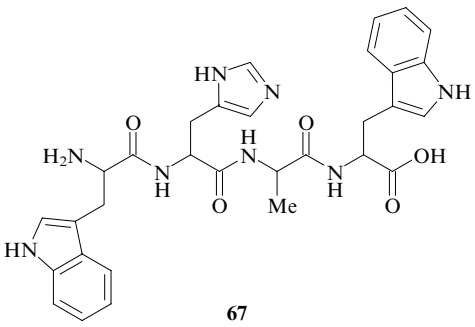


Figure 36. Polydiacetylene–tripeptide **67** vesicles on the surface of carbon nanotubes used for the detection of TNT.[245]

nanotubes (SWNT) as a part of a nano-sized field effect transistor under UV radiation (Fig. 36). The device thus fabricated showed unprecedented (down to 1 fmol litre^{-1}) sensitivity to TNT, which was manifested as a change in the electrical conductivity.[245]

Structure 67



67

IV. Conclusion

The material presented in the review convincingly demonstrates that low-molecular-mass chemical sensors (chemosensors) and materials based on them are currently a fully featured analytical tool for the detection of nitroaromatic compounds (explosives) in air, water and soil and on the surfaces of items.

Visual (colorimetric and photoluminescent) detection methods remain most widely used. The key advantages of these methods are versatility, the absence or a minimum number of false readings, high speed (the result is available in a minute or less), portability (no cumbersome equipment is needed and, in most cases, the assay can be performed on site). The key driving force of the visual detection of nitroaromatic compounds (explosives) is the formation of a covalently bonded product or non-covalently bonded molecular complex between the electron-withdrawing nitro compound (analyte) and electron-donating chemosensor (reagent, sensor or indicator). This reaction gives rise to an intense colour, static or dynamic fluorescence quenching and/or change in the luminescence characteristics of the sensor, or, in very rare cases, enhancement of the chemosensor photoluminescence (fluorescence).

Among the electrochemical (electrical) methods for the detection of nitro compounds, most widely used are methods relying on appropriately chemically or mechanically premodified electrodes. Targeted synthetic or mechanical design of chemosensors and sensing materials deposited on the electrode surface to increase the selectivity ensures effective recognition of a nitroaromatic explosive with high reliability.

To summarize the foregoing, it can be stated that many of the described chemosensors are ready for use in sensing components of electronic devices, which in some cases already replace sniffer dogs. Subsequently, the targeted modification of the sensing elements of these devices, in particular, by the design of new hybrid materials (to increase the affinity of sensing elements for analytes) and the use of nanotechnologies (to increase the active mass exchange surface area of sensing elements) would give rise to a new generation of multifunctional detector devices with potential far beyond the possibilities of sniffer dogs. In particular, these devices would be able to detect and recognize a broad range of nitroaromatic compounds (explosives) in air, water, soil and on the surfaces of items even in the presence of competing compounds and solvents.

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