

Organic Optoelectronic Materials for Trace Explosive Sensing

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Abstract: Detection of trace explosives is of great concern for homeland security, battlefield protection, and industrial and environmental safety control. Fluorescence quenching based sensing has proven to be one of the most promising approaches for trace explosives detection. This review is focused on examples reported by Prof. Ling Zang's group and Prof. William Trogler's group related to fluorescence quenching sensors based on one-dimensional small molecular nanomaterials, fluorescent coordination polymers (or metal-organic frameworks) and polysiloles. It is also introduced the use of organic semiconductors, such as phthalocyanine thin films and perylene diimide nanowires, to construct electronic sensors for trace explosive sensing.

Key words: explosive sensing; sensor; fluorescent compounds; trace detection

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1 Introduction

Nowadays a lot of attention is being paid on the development of methods and instrumentation for the detection of explosives and illicit chemicals, because of the threat of terrorist use of explosive device and chemical, biological or radioactive agents^[1-5]. Additionally, the analysis of explosives is also of great importance for environmental cleaning, forensic science and military operations^[6]. Many techniques have been investigated for the detection of explosives, such as gas chromatography coupled with mass spectroscopy, nuclear quadrupole resonance, energy dispersive X-ray diffraction, neutron activation analysis, electron capture detection, ion mobility spectrometry, and cyclic voltammetry^[7,8]. Most of them, though highly sensitive, are expensive and require sophisticated instrumentation that is not easily applied to on site field testing. For the large area searching or personal control, sniffer dogs are the most successful explosives detection systems at present. On the other hand this method is not

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well-suited for continuous monitoring because dogs are living beings and show behavioral variations. So improvements of existing sensor platforms along with development of new chemical sensors are always needed.

Explosive compounds can be classified according to their chemical structures^[5,7]. The chemical structures of some common explosives are shown in Figure 1. These include the nitroaromatics such as trinitrotoluene (TNT), picric acid (PA), and 2,4,6-trinitrophenylmethyl nitramine (Tetryl); and nitroalkanes such as nitromethane and 2,3-dimethyl-2,3-dinitrobutane (DMNB, tagging/detecting agent for plastic bonded explosives); and nitramines such as 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX); and nitrate esters such as pentaerythritol tetranitrate (PETN); and peroxides such as TATP. One property of the nitro explosives which may be exploited in detection schemes is their electron accepting capability^[4]. The electron deficient molecules are able to form complexes with electron rich fluorophores, which has been widely used to detect them via electron-transfer-induced fluorescence quenching. While, peroxide-based explosives have a strong oxidant character, which has been used to design fluorogenic and chromogenic probes based on redox reactions coupled by color/emission changes^[5,9,10].

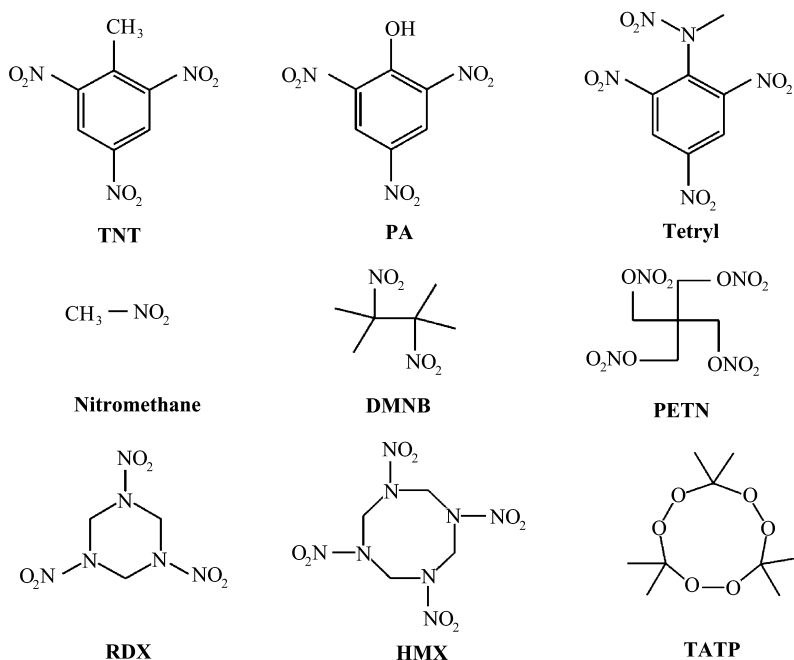


Figure 1 Chemical structures of common explosives

Substitution of the electron-withdrawing nitro groups make the explosive molecules highly electron-deficient and readily to accept electrons from excited fluorophores.

Electron-transfer-induced fluorescence quenching is the most practical and efficient mechanism of signal transduction for the detection of explosives. A basic frontier molecular orbital based mechanism for electron transfer fluorescence quenching is illustrated in Figure 2^[2]. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the electron donor (fluorophores) and acceptor (nitro explosives) are illustrated in this simple diagram. In the ground state of donor and acceptors, electron transfer reaction cannot be happened because there is no energetic driving force. When a fluorophore is excited by UV/Vis radiation, an electron is promoted into a higher energy states (LUMO). In the absence of an acceptor, a photon is emitted when the fluorophore relaxed back to the ground state, resulting in the emission of light. Otherwise, because of the LUMO of acceptor is lower in energy than the LUMO of donor, there is a significant energetic driving force to lower the energy of the system via an electron transfer from donor to acceptor, resulting in oxidation of donor and concomitant reduction of acceptor, giving an ion radical pair. Because the singlet excited state of donor has been transformed in this reaction, it can no longer emit, and typically the fastest process is simple reverse electron transfer from the LUMO of acceptor to singly occupied HOMO of donor, which is non-radiative in nature.

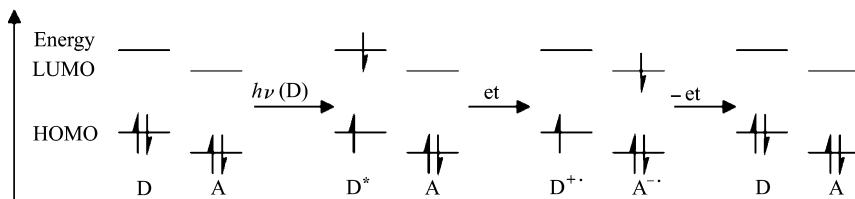


Figure 2 A molecular orbital diagram for photoinduced charge transfer (“et” refers to electron transfer; “-et” refers to reverse electron transfer)^[2]

In principal two major approaches to detect explosives can be distinguished; bulk detection and trace detection^[11]. Bulk detection of explosives is very common, e. g. , in airport security. Usually, explosive material is detected directly by viewing images made by x-ray scanners or similar equipment. In trace detection, the explosive is detected by chemical identification of microscopic residues of the explosive compound. These residues can be in either or both of two forms; vapor and particulate. Vapor refers to the gas-phase molecules that are emitted from a solid or liquid explosive because of its finite vapor pressure. Particulate contamination refers to microscopic particles of solid material that adhere to surfaces that have, directly or indirectly, come into contact with an explosive material. Trace detection of explosives is not easy. One reason is the low vapor pressure of most explosives. Figure 3 shows a few commonly used high explosives and their vapor concentration in saturated air^[11,12]. Some of the

explosive, such as EGDN and DNT, having saturated vapor concentrations in air close to or greater than one part per million (1 ppm), can be seen as volatile or high vapor pressure explosives. The low-vapor-pressure explosives, such as HMX, RDX and PETN, have saturated vapor concentrations in air near or below the one part per trillion (1 ppt). They can be seen as non volatile particles and are almost impossible detected in vapor phase. TNT, one of the more ubiquitous explosives used, has a moderate vapor pressure (approximately 5 ppb at room temperature) and is possible to be detected both in vapor phase and in solid.

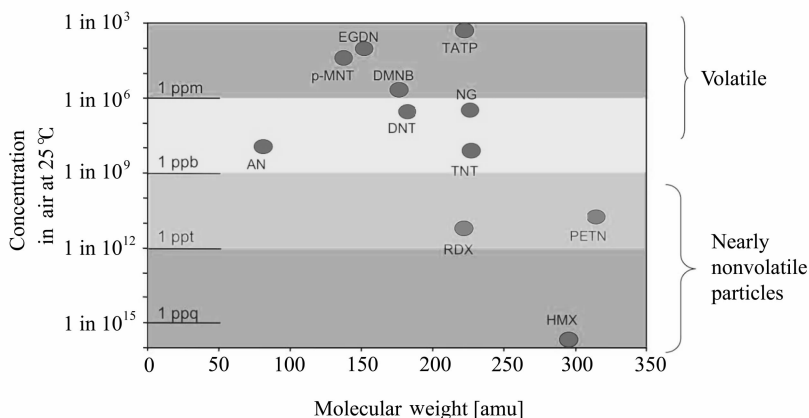


Figure 3 Vapor concentrations of high explosives in saturated air at 25 °C^[12]

Chemical sensors can be broadly classified as optical sensor or electronic sensor based on optical or electronic readout mechanisms. Due to the importance and widespread interests of explosive sensing, several review articles with emphasis on different aspects have been published^[2-5,13-16]. This review will focus on research works of Prof. Ling Zang's group and Prof. William Troglor's group at University of Utah and University of California, San Diego, respectively. We will briefly introduce the optical sensor via fluorescence quenching based on one-dimensional small molecular nanomaterials, fluorescent coordination polymers and polysiloles. Then we will demonstrate the researches on electronic sensors based on semiconductor phthalocyanine thin films or organic photoconductive nanowires.

2 One-dimensional small molecular nanomaterials

While the detection of explosives in the vapor phase can be a difficult task, it must be said that there are some very good, reliable sensors that operate by vapor phase detection. The pentiptycene based conjugated polymer sensor developed by the Swager group is an example of a very sensitive vapor phase sensor (Figure 4)^[15-18]. A conjugated polymer can be seen as a "molecular wire" because each repeat unit in the

exposure to air or quickly recovered by exposure to the vapor of hydrazine (Figure 5B).

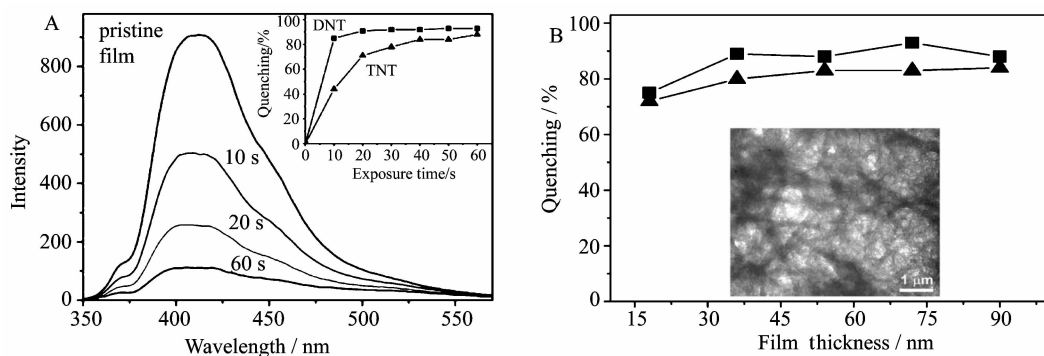


Figure 5 (A) The fluorescence of ACTC film was quenched by a saturated vapor of TNT (5 ppb) at various time. The inset showed the time-course of quenching for TNT and DNT
(B) Thickness dependence of fluorescence quenching efficiency of ACTC films

The quenching was tested upon exposing the film to saturated vapor of TNT (▲) and DNT (■) for 60 s. The inset is a TEM image of a thin film of ACTC cast on silicon oxide from 2 mmol/L THF solution [20].

However, both pentiptycene conjugated polymers and ACTC impose much difficulty to synthesis because they require multistep synthetic process and/or special catalysts for making the precursors. Recently, Zang's group reported 2,7-linked carbazole trimer can be synthesized in one-step by Suzuki-coupling reaction (Figure 4) [22]. The nanofibril film of carbazole trimer demonstrated the same efficient, fast fluorescent sensing for nitroaromatic explosives (*e.g.*, TNT, DNT) as ACTC film. Furthermore, the sensor also showed good response to nitroaliphatic explosives (*e.g.*, nitromethane), which remain difficult to detect due to their high volatility and low chemical binding to many sensory materials, and implied the potential applications for on-site explosive monitoring.

3 Fluorescent coordination polymers

Coordination polymers, or metal-organic frameworks (MOFs), constructed from metal ion connectors and polydentate bridging ligands, have drawn growing interest in chemistry and materials science due to their unique and highly tailorable properties and potential applications in heterogeneous catalysis, drug delivery, imaging, and sensing [23-25]. Fluorescent MOFs have good potential to sense explosives because of porosity, high surface area, which may allow more analyte molecules to come into contact with the MOF surface and may reach high sensitivity [26,27].

Prof. Jing Li's group reported that highly luminescent microporous crystalline metal-organic framework (MMOF) [Zn₂(bpdc)₂(bpee)], can be able to highly

sensitively detect nitroaromatic explosive DNT and plastic explosive taggant DMNB^[26]. The outstanding sensing capability may be attributed to the infinite 3D framework structure and inherent microporosity. The network structure of MMOF, containing π moieties, may also facilitate the excitons migration like conjugated polymers. Their latest work demonstrated a possible way to selectively detect explosives of different types (eg, aromatic DNT vs aliphatic DMNB)^[28].

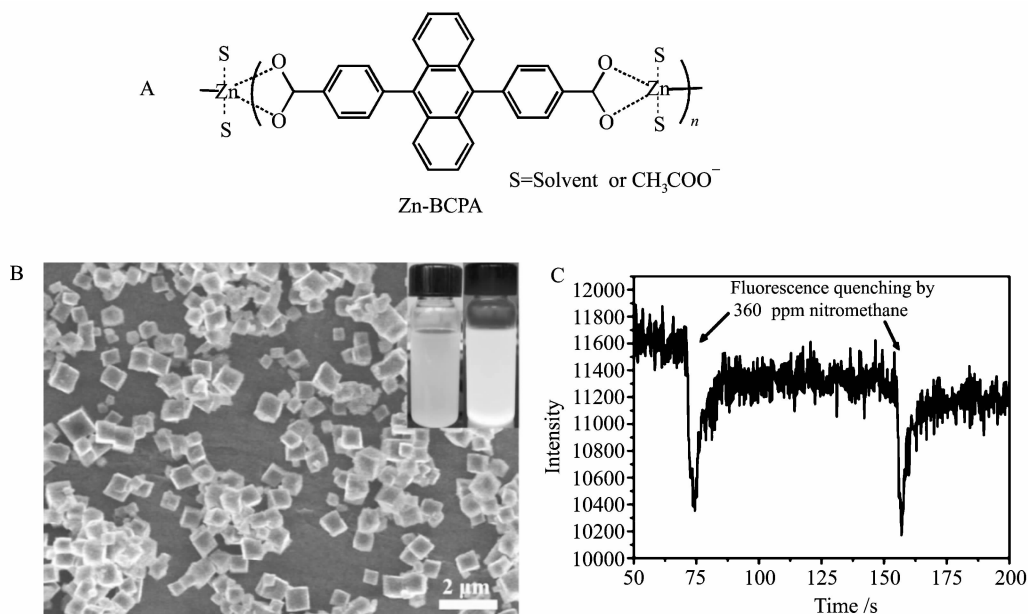


Figure 6 (A) Molecular structure of Zn-BCPA coordination polymer
(B) SEM image of Zn-BCPA nanocubes (Insets are the photoimages of Zn-BCPA NCPs under daylight and UV illumination at 354 nm respectively)
(C) Emission intensity as monitored at 450 nm for a film of Zn-BCPA NCPs upon blowing over with 360 ppm nitromethane vapor^[29]

Scaling down these materials lead to highly tailorable nanomaterials know as nanoscale coordination polymers (NCPs)^[30-32]. Zang's group reported a nanoscale zinc (II)-carboxylate coordination polymers with a π -conjugated ligand (Zn-BCPA)^[29]. The nanomaterial has a cubic morphology with strong fluorescence and efficient emission quenching upon interaction with the nitro-based explosives including DNT, TNT and the high volatile nitromethane (Figure 6). For example, when Zn-BCPA NCP film was blew over by nitromethane vapor with a concentration as low as 360 ppm (1% of saturated nitromethane vapor in air), its emission intensity was quenched by 10%, monitored by a portable spectrometer, which make them promising sensory materials for infield explosives monitoring.

4 Polysiloles

Silole is one kind of metallacyclopenta-2,4-dienes, or metalloles, which are analogous to cyclopentadiene but have a Group 14 (IVA) element (Si, Ge, Sn, Pb) substituted at the sp^3 carbon^[4]. As seen in Figure 7, low lying σ^* orbitals of the silicon atom have a favorable overlap of that of the π^* orbitals of cyclopentadiene organic framework. This favorable interaction produces fluorescence with relatively low energy excitation states. Polysiloles possess the same features including a low reduction potential, low lying LUMO and visible fluorescence. These make the polysiloles ideal sensing materials via fluorescence quenching with amplification effect due to electron delocalization in these polysiloles.

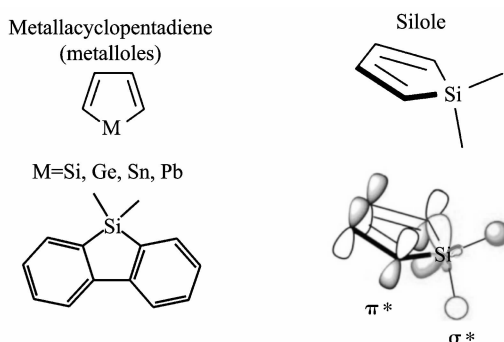


Figure 7 Molecular structures of metalloles, silole and silafluorene^[33]

Trogler's group has deeply researched the synthesis of polysiloles and their sensing applications^[9,33-38]. Detection of nitroaromatic explosives, such as DNT, TNT and PA, was explored in organic or aqueous solution. Besides that, one of the most interesting works was fluorescence sensing for explosive particulate. As we have described above, some of common high explosives, such as, PETN, RDX and HMX, have very low vapor pressure (near or below 1 ppt) at room temperature. Considered the environmental surfaces will also trap vapor molecules, the amount in the vapor phase will even lower. These promoted researcher to look upon particulate as target analytes. Whatever in solution or vapor phase, the sensing system requires the analyte to have effective interaction with sensor. The advantage of their detection as particulate or in the solid state is that the affinity for the sensor can be eliminated.

Sohn, *et al* first demonstrated surface detection method for the analysis of solid particulates of TNT^[38]. A polysilole thin layer was coated by spray-coating onto filter paper or other substrates which were contaminated with TNT. Then the substrate can be illuminated with a small ultraviolet (UV) lamp, while TNT residue will quench luminescence on the substrate. The quenched area could be easily distinguished from the region unaffected by naked eyes, which make trace residue of TNT visualize. The

explosives studied by this detection method were expanded to include PA, RDX, HMX, Tetryl, TNG, and PETN^[33,34,39]. And the detection limits are reported in nanograms per square centimeter to emphasize the quantity of explosive deposited in the given area. Some examples of this method can be seen in Figure. 8, where various amount of RDX were deposited onto filter paper, tetryl was deposited in ceramic wells, and PETN successive thumbprints were all visible after a polysilole solution was applied. The improved method has negated the vapor pressure issue and allowed for the detection of high explosives that were previously not attainable.

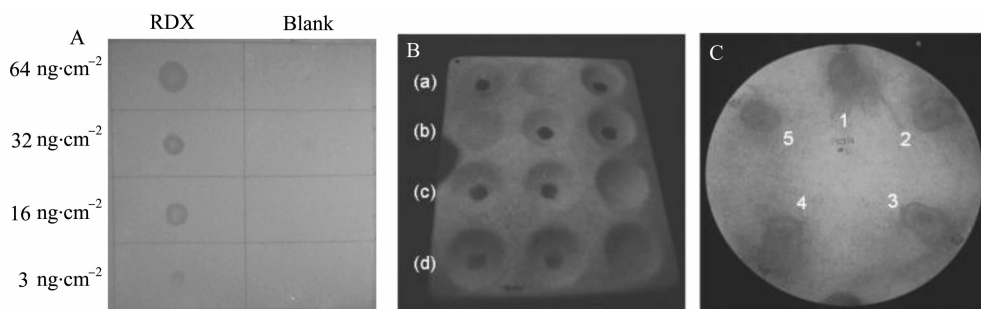


Figure 8 Examples of fluorescence quenching of thin films of silafluorene polymers by solid particulates of various explosives imaged with a Sony 2.0 megapixel digital camera under continuous UV excitation (302 nm)

(A) Detection of RDX particulates on filter paper

(B) Detection of tetryl particulates (a) 64, (b) 32, (c) 16, and (d) 3 $\text{ng} \cdot \text{cm}^{-2}$ on a porcelain tray.

The analyte was randomly placed in 2 of 3 wells, and observed quenching was confirmed by an independent observer

(C) Detection of five successive thumbprints on filter paper contaminated with production-line PETN particulates^[33,34]

5 Explosive detection via electronic sensor

Sensors that convert a chemospecific sensing event into a voltage or current output are broadly classified as electronic sensors^[40]. The advantages of electronic sensors are their low power requirements, sensitivity, and easy integration for sensor arrays, while the issues such as selectivity and stability baffled their practical applications. The electronic sensor types would include resistive, capacitive, surface acoustic wave (SAW), electrochemical, and mass (*e. g.*, quartz crystal microbalance (QCM) and microelectromechanical systems (MEMSs)). The sensitivity and selectivity of sensors rely on the materials designed, which will change their electronic properties in specific ways when in contact with volatile compounds.

Although photoluminescent sensors have been seen as most efficiency for explosive sensing as we described above, improvised peroxide explosives cannot be detected in this way. Recent incidents in England and Germany involving peroxide based explosives have made peroxide detection crucial to counterterrorism efforts. Vapor phase

monitoring of peroxides has been a topic of critical importance. As reported by Trogler's group, chemiresistors based on thin films of metal phthalocyanines (MPcs, $M = \text{Co}, \text{Ni}, \text{Cu}, \text{and H}_2$) are examined as sensors for vapor phase H_2O_2 detection under practical conditions (*i. e.*, in the presence of ambient humidity) (Figure 9A)^[41]. Selectivity is gained from the ability of H_2O_2 to cause current losses in CoPc sensors and current gains in NiPc, CuPc, and H_2Pc sensors (Figure 9B,C). The reason for large current losses is that cobalt-catalyzed oxidation of H_2O_2 on the surface of CoPc is occurring (with concurrent film reduction), leading to hole trapping and loss of current. In contrast, MPcs with nonredox-active metal centers ($M = \text{Ni}, \text{Cu}, \text{and H}_2$) were revealed no electrocatalytic behavior in the presence of H_2O_2 . However, small amount of hydroxyl radicals were generated, leading to the observed sensor response as radical reaction or as charge-transfer processes.

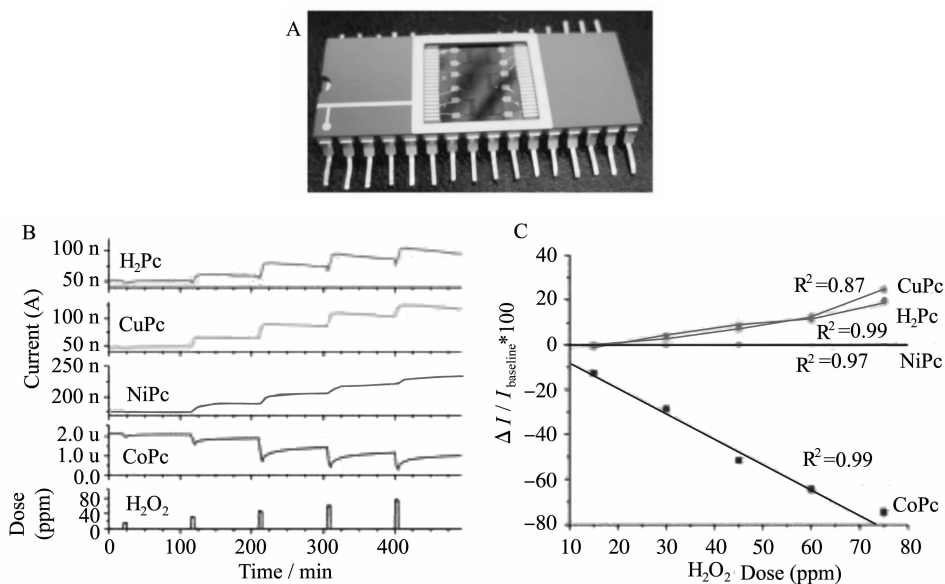


Figure 9 (A) MPc sensor array containing six chemiresistors wirebonded in a dual-inline ceramic package (B) Sensing data for MPcs ($M = \text{Co}, \text{Ni}, \text{Cu}, \text{H}_2$) exposed to varied concentration doses of 27% H_2O_2 (aq) (C) Quantitative sensor response data plotted for each dose in (B)^[41]

This is the first example of contrasting analyte redox behavior dependent on the MPc metal center in a chemiresistor. Due to its high catalytic activity, CoPc is the most sensitive material for detecting H_2O_2 , with a detection limit of 50 ppb, much better than that of commercial H_2O_2 sensors (in the range of 0.1 to 1 ppm). And the research on ChemFETs based on vapor deposited or solution-processed phthalocyanine thin-films is ongoing to detect organic peroxide (such as TATP).

Zang's group also reported an electronic sensor based on organic nanoribbons for

nitro explosive sensing^[42]. The nanoribbons were self-assembly from soluble perylene diimide (electron acceptor) with various donor groups (Figure 10). Their

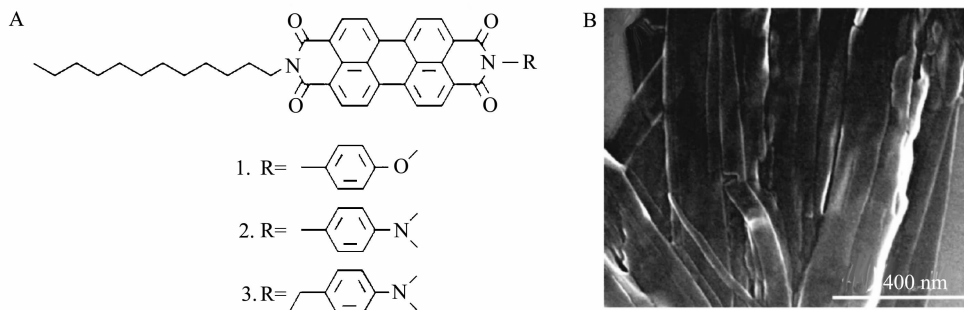


Figure 10 (A) Molecular structures of perylene diimide with various electron donor groups
(B) SEM images of nanoribbons fabricated from molecular 3^[42]

photoconductivity is much higher than dark current because the good kinetic balance between the intramolecular charge recombination (between D and A) and the intermolecular charge transport along the nanoribbon. The photogenerated electrons can be efficient trapped by oxygen molecules or other oxidizing molecules (such as nitro compounds), leading to depletion of the charge carriers or current loss. Having these findings, the authors constructed the electrical vapor sensors that relies on the photocurrent modulation and takes advantage of the enhanced gas adsorption intrinsic to the porous nanofibril film, and proved to be effective sensing nitro-based explosives, including nitromethane, nitrobenzene, 4-nitrotoluene, and 1-chloro-4-nitrobenzene. Furthermore, the sensors have negligible current response to many other common solvents and some reductive reagents such as aniline. That demonstrated the good sensing selectivity.

6 Conclusions and future perspectives

Besides Zang's group and Troglor's group, a few groups are active in the explosive sensing research, which promoted the development of commercial products^[43-46]. Due to the advantages of fluorescence quenching method and the signal amplifying effect of conjugated molecules, portable trace explosive sensors based on polysiloles and small molecular nanofibrils have been fabricated with the commercial name "RedX Defence XPAK" and "Vaporsens", respectively^[47,48]. As most fluorescence quenching sensors are limited to nitroaromatic-based explosives, trace detection of other classed (*e. g.*, nitramine, nitrate, and peroxide) with low vapor pressure is still a challenge. And optical sensor based on "turn-on" mechanism remains an area in need of further progress. Very recently, sensors based on luminescent MOFs have attracted a great

deal of attentions because the luminescent properties are highly sensitive and potentially selective to guest species.

Electronic sensors are valued for their low power requirements, sensitivity, and potential for mass fabrication in a compact form. The technology for measuring voltage and current is highly sensitive and of low cost, which makes such sensors attractive as compact inexpensive sensors. However, issues such as chemical sensitivity, selectivity, and stability pose challenging practical barriers to their application.

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基于有机光电材料的痕量爆炸物识别

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摘 要: 随着国际恐怖袭击事件的增多, 痕量爆炸物的识别技术研究越来越为重要. 本文以作者在该领域的研究为例, 综述了基于一维有机纳米材料、荧光金属配位聚合物(金属-有机框架化合物)和聚噻咯的荧光猝灭技术, 在痕量爆炸物识别上的应用. 同时介绍了酞菁薄膜和菲亚酰胺纳米线制备的电子传感器分别对过氧化物和硝基类爆炸物有灵敏的响应.

关键词: 爆炸物识别; 传感器; 荧光化合物; 痕量检测

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