

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Nanoscaled Fluorescent Films and Layers for Detection of Environmental Pollutants

Meizhen Yin and Chendong Ji

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/67869>

Abstract

Hazardous gas and ion pollutants are the most serious environmental problems around the world. It is of great importance to develop devices for easy detection of these hazardous substances. Fluorescence technology with high resolution and operational simplicity has attracted a lot of attention in recent years. Organic fluorescent dyes absorb/emit lights within a broad wavelength range, which is suitable for various demands. Chromophores, such as perylene, cyanine dyes, spiropyran, and so on, are widely studied as fluorescent probes for gases and ions. The dyes could respond to external stimuli through structural changes of the conjugated chromophore itself or the attached functional groups, leading to detectable spectral changes. Organic dyes are incorporated into nanoscaled films and layers, which are portable and durable for effective sensing in complex environments. In this chapter, preparation and application of fluorescent films and layers (FFL) for gaseous/ionic detection are reviewed. We discuss the response mechanism of fluorescent dyes, the fabrication of nanoscaled FFL, and some examples of FFL for the detection of gas and ion pollutants.

Keywords: environmental pollutants, detection, fluorescence, nanoscaled films and layers, gases/ions sensor

1. Introduction

Human activities have introduced increasingly hazardous pollutants into the environment since the growth of industry, agriculture, and livestock. These pollutants including toxic gases and trace element ions caused pollutions of atmosphere, water, and soils, which severely harm the existence and development of human beings [1]. Thus, effective and inexpensive systems for detection and quantification of environmental pollutants have been progressively

more important. Currently, conventional detection methods are based on chromatography-mass spectrometry (GC-MS), electrochemical systems, and spectrophotometers [2–4]. In these processes, large stationary instruments and complex components are required, which limit their use in resource-limited fields. Thus, there is currently a global effort to develop new technologies to evaluate and detect these environmental pollutants.

In recent years, fluorescence technology (FT) with high resolution and operational simplicity has attracted a lot of attention [5]. Taking advantage of FT, sensors based on chromophores have been considered promising alternatives for environmental measurements due to their simplicity, high sensitivity, and inexpensive nature. Particularly, organic fluorescent dyes are widely studied because they absorb/emit lights with a broad wavelength range, which could fulfill a variety of demands [6, 7]. Functionalized organic dyes could respond to external stimuli through structural or morphological change, which leads to the change of their apparent colors and fluorescence signals. It's worth mentioning that the response is easy to check by naked eye or using ultraviolet (UV) lamp. Therefore, design strategies to chemosensors for effective detection of environmental pollutants have attracted significant attention over the past few years.

On the other hand, recent developments in the field of nanotechnology have triggered increased interest in using nanomaterials for environmental applications [8]. Nanoscaled films and layers possess unique properties that can be used to improve the performance of existing sensors. Organic dyes are incorporated into self-supported films and layers as fluorescent films and layers (FFL) that are portable and durable for effective sensing in complex environments. Furthermore, taking advantage of their nanoscaled dimensions and controllable surface, FFL perform high sensitivity and selectivity to the analyte, which could be regarded as a promising sensing material especially for hazardous pollutants.

This chapter focuses on the recent developments of nanoscaled FFL for the detection of environmental pollutants. We first begin with the sensing mechanism of synthetic dyes and the fabrication of FFL based on these dyes. Then, some examples of FFL for the detection of gaseous pollutants (such as CO_2 , NH_3 , and HCl gas) and metal ions (such as Hg^{2+} , Pb^{2+} , and Cd^{2+}) is discussed.

1.1. Sensing mechanism of synthetic dyes for environmental applications

The main hurdle for fluorescent techniques lies in the construction of fluorescent sensors with high selectivity, sensitivity, and stability. Taking advantage of their structural designability, easy synthesis/modification, and high fluorescence quantum yields [9], organic sensors have become a new multidisciplinary research field involving organic synthesis, analytical chemistry, and environmentology. For environmental applications, different chromophores with various response mechanisms have been developed for the detection of hazardous pollutants. Herein, we present a survey on recent progress in sensing strategies of organic chromophore for the detection of hazardous gases and ions.

Organic dyes with aromatic structure, such as rylene dye and cyanine dye, emit strong and stable fluorescence but easily aggregate due to strong π - π stacking interaction [10]. For the

modification of these dyes, gas/ion responsive groups are attached to the periphery of the conjugation structure. The structural changes of functional groups usually affect the electron distribution or aggregate state of the fluorophores, resulting in distinct changes in the absorption/fluorescence spectrum. Based on organic dyes, a number of photophysical signaling mechanisms for sensing have been developed, such as photoinduced electron transfer (PET) [11, 12], intramolecular charge transfer (ICT) [11, 12], fluorescence resonance energy transfer (FRET) [13], and aggregation-disaggregation effect. In addition, different mechanisms of aggregation-induced signal change including aggregation-caused quenching (ACQ) [14] and aggregation-induced emission (AIE) [15] are studied for sensing environmental pollutants. The sensing strategies of fluorescent dyes are concluded in **Table 1**.

PET with “fluorophore-spacer-receptor” format is the most commonly exploited approach for designing fluorescent sensors and switches. Herman et al. reported an approach for sensing carbon dioxide based on PET (**Figure 1**) [16]. In this case, sensor **1** is nonfluorescent or weakly fluorescent due to the quenching by amine group through PET process. Upon reaction with CO₂, the basic amine group forms a carbamate salt and a positively charged ammonium group, resulting in prevention of the PET process, after which a turn-on fluorescent response is predictable.

Methods based on energy transfer (ET), such as FRET, hold great promise for pollutant detection, allowing precise and quantitative analysis and imaging even in complicated systems. Kim et al. reported a calix[4]crown chemosensor **2** based on dual sensing probes revealing high selectivity for Pb²⁺ ion over other metal ions (**Figure 2**) [17]. Sensors containing calix-crown molecules with a diazo group giving a visual color change and a pyrenyl group providing a fluorescence change were constructed. By Pb²⁺ ion complexation, the sensor performed fluorescence enhancement due to diminished FRET effect.

ACQ and AIE dyes are both developed as sensing materials with “turn-off” or “turn-on” models. Yin et al. reported a selective fluorescent chemosensor based on ACQ dye **3** for recyclable

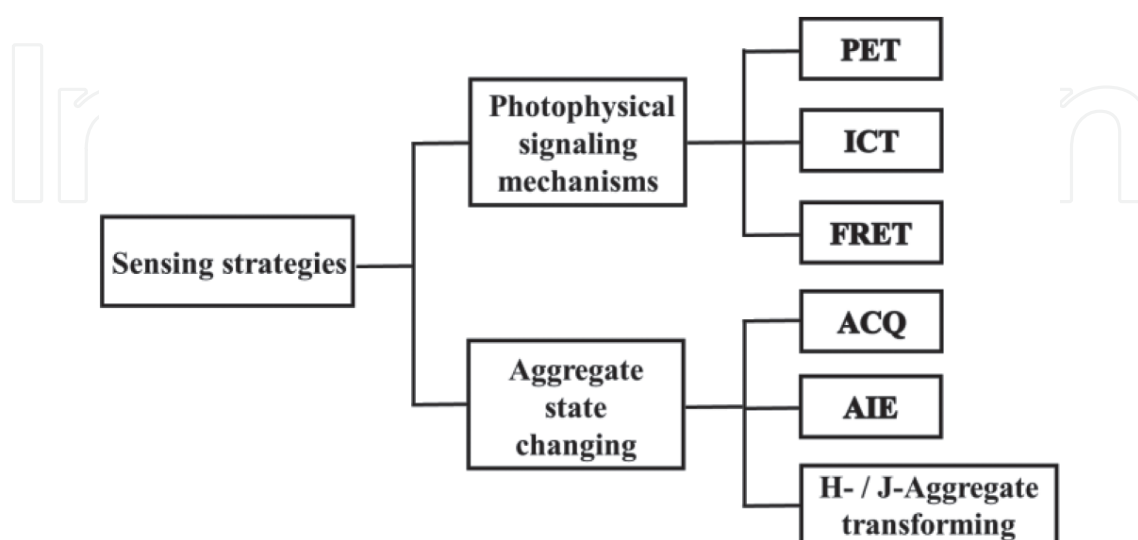


Table 1. Sensing strategies of the chromophores containing responsive groups.

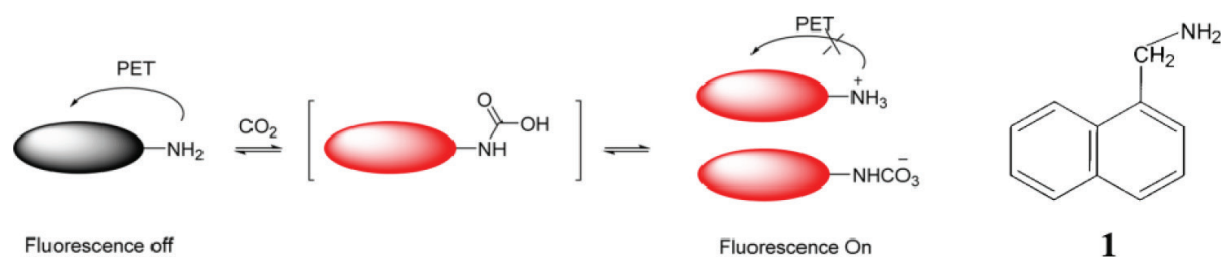


Figure 1. Strategy of PET-based chemosensor for CO_2 and chemical structure of **1**.

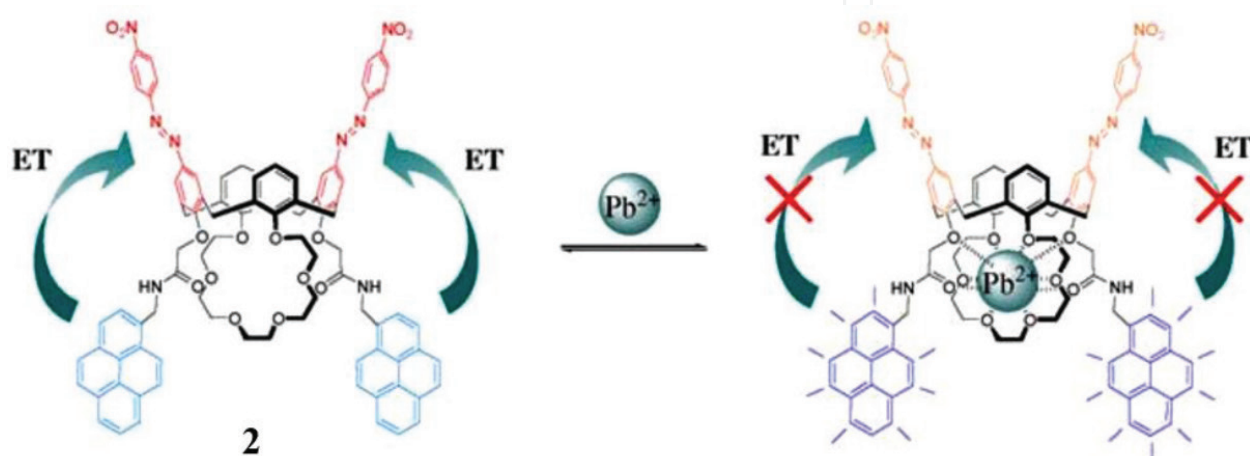


Figure 2. Sensing mechanism of probe **2** with Pb^{2+} . Copyright 2005 Elsevier B.V. All rights reserved. The aggregate state of dyes exerts a tremendous influence on their spectral properties.

Hg^{2+} detection with high sensitivity (Figure 3) [18]. With the addition of 20 mM of Hg^{2+} , the fluorescence of **3** (5 mM) is quenched completely.

Tang et al. reported a simple approach for quantitative detection of CO_2 gas with an AIE chromophore hexaphenylsilole (**4**, HPS) [19]. **4** is nonradiative in the very dilute dipropylamine (DPA) solution ($\sim 37 \mu\text{M}$) due to the restriction of intramolecular motion (RIM) mechanism (Figure 4a). Bubbling DPA liquid with CO_2 gas results in the formation of a viscous and polar carbamate ionic liquid (CIL) with poor solvating power toward **4** (Figure 4b). The molecule **4** aggregates in CIL and exhibits the “turn-on” fluorescence as a CO_2 sensor.

Another strategy taking advantage of the self-association of dyes is also investigated. The aggregation of dyes also strongly affects their spectroscopic characteristics, and these spectral changes can be attributed to aggregation of the dye molecules in water to form dimers and higher order aggregates in the “J-” or “H-” type aggregation state [20]. Yin et al. developed a self-assembled fluorescent film by carboxylic acid group functionalized squarylium cyanine dyes **5** [21]. **5** in the solid state showed selective response to ammonia gas due to its unique molecular aggregation and size effect of ammonia molecule. The aggregated **5** could transit from J-aggregation to H-aggregation upon ammonia treatment and easily recovered by the treatment with HCl gas (Figure 5).



Figure 3. Synthesis approach and sensing mechanism of chemsensor 3.

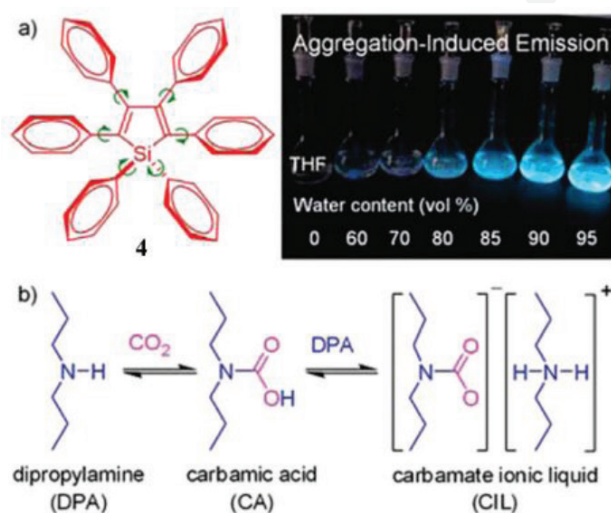


Figure 4. (a) Dye 4 is nonemissive when dissolved in THF but becomes strongly fluorescent when aggregated in THF/water mixtures with high water contents. (b) Formation of CIL by bubbling CO_2 gas through DPA liquid. Copyright 2007 American Chemical Society.

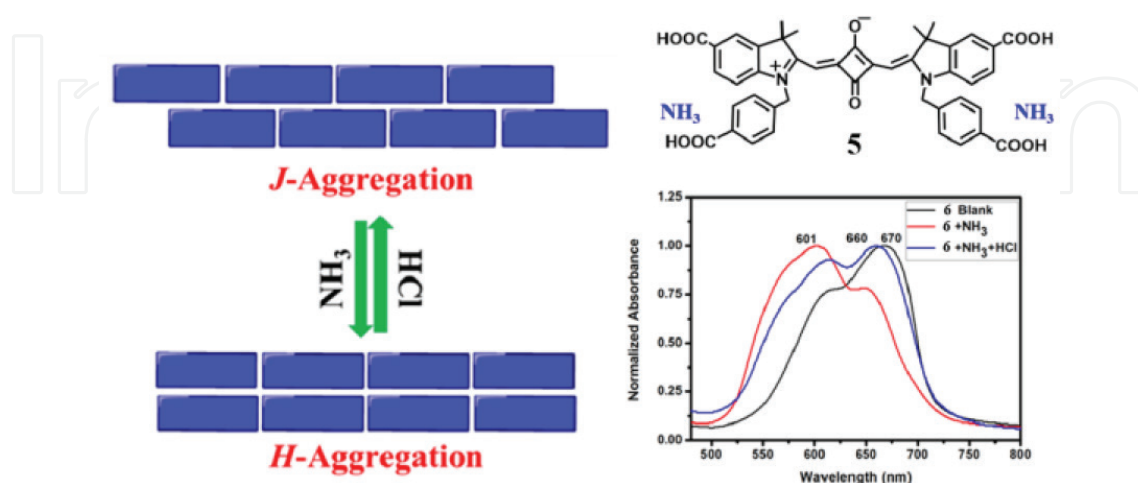


Figure 5. The mechanism of concentration-dependent self-assembly of dye 5 in the solid state for selective ammonia sensing.

1.2. Fabrication of films with organic dyes

Pollutant detection is challenging in atmosphere, water, and soil because of the complex components and rigorous conditions. Although organic dyes are sensitive to specific analytes, their applications in real environment are still limited due to their unstable nature. Nanomaterials have many excellent properties, such as strong adsorption, fine and tunable nanostructure, and stability [22]. The combination of organic dye and nanotechnology could maximize the functions of dye, while resulting in functional materials with higher performance. Nanomaterials with various architectures, such as particle, film, and layer, have been widely applied as sensors for environmental monitoring and pollutant detection. Film sensors have attracted enormous attention due to easy preparation, good applicability, and portable properties. In the chemosensory processes of films, the physical or chemical interactions occur at the surface or interface of the materials. Thus, controlling of the specific surface area, surface energy, and surface chemistry of films and layers through nanotechnology is of great importance. For example, compared with bulk materials, nanofibers with high surface area to volume ratio possess higher functional group density. Porous films also have high surface area and ordered porosity. These unique characters lead to higher sensitivity of the nanoscaled films and layers [23].

Advances in nanoscaled FFL are providing unprecedented opportunities to treat pollutants in environment. During the fabrication of FFL for pollutant detection, the following four precedent conditions should be met: (1) environment security, (2) reuse of sensors, (3) low cost, and (4) high detection efficiency. Based on these concerns, polymer films with dyes doped or embedded were widely used as sensing fluorescent films.

1.2.1. Casting films

Casting films were prepared by doping organic dyes into matrix polymers directly. The solvent mixture of dye and polymer was spread into a thin layer and then air-dried to prepare the film. The film is conveniently manufactured into devices and easily tailored according to practical need, which is widely adopted in the field of environment monitoring [24–27].

1.2.2. Cross-linking films

As polymer is an ideal supporting material for organic sensing molecules, efforts have been made to further improve its stability and mechanical strength. Polymer networks could achieve stronger intermolecular interactions, closer molecular packing, and reduced polymer mobility by means of cross-linking using physical or chemical treatments [28]. Therefore, cross-linking has been explored as a viable method to improve the properties of polymer films as well as to give a stable environment for the embedded dyes.

Yin et al. reported a series of cross-linked fluorescent polyvinyl pyrrolidone (PVP) films covalently attached with different perylene derivatives (PDA, 4Cl-PDA, and 4Cl-PDI) (**Figure 6**) [29–31]. The ring-opening reaction of anhydride end groups and aromatic nucleophilic substitution

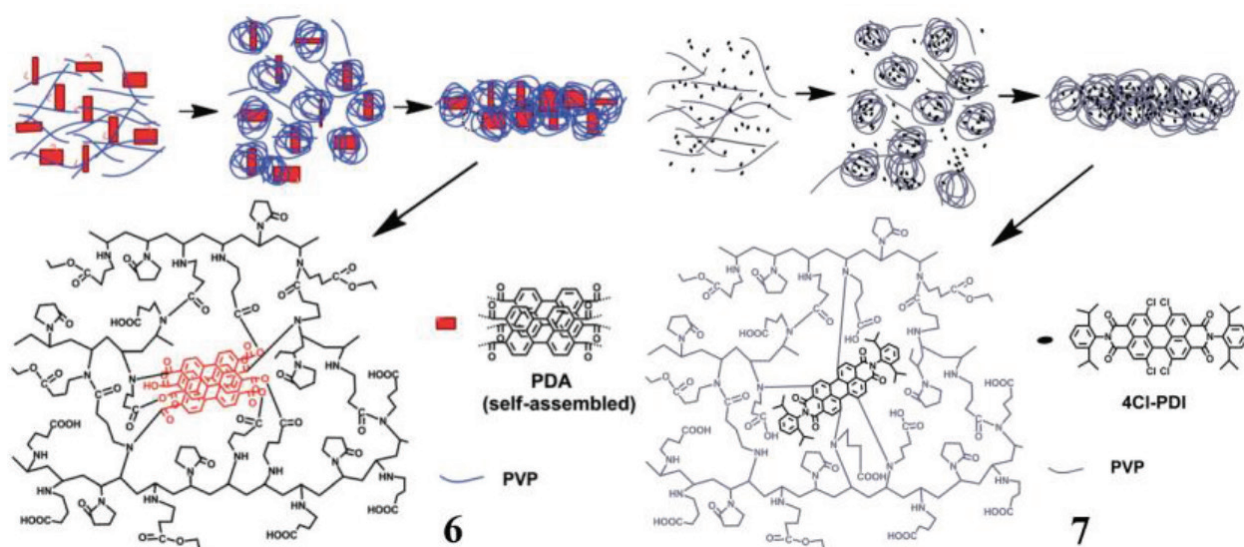


Figure 6. Formation of the fluorescent PVP films 6 and 7 based on perylene derivatives.

between the chlorine atom and the secondary amine in PVP both contributed to the PVP-chromophore conjugation. The obtained fluorescent film 6 and 7 showed highly stable optical performance originated from perylene chromophore.

1.2.3. Layer-by-layer (LbL) assembled films or layers

The LbL method has been reported to be a useful method for the preparation of molecularly assembled films. It was introduced in 1966 by Iler [32], and subsequently extended by Decher and coworkers to encompass the alternate adsorption of polycations and polyanions onto a surface [33]. A versatile approach for preparing nanoscaled thin film by LbL method is shown in **Figure 7** [34]. A substrate with inherent charge is first exposed to an oppositely charged polyelectrolyte,

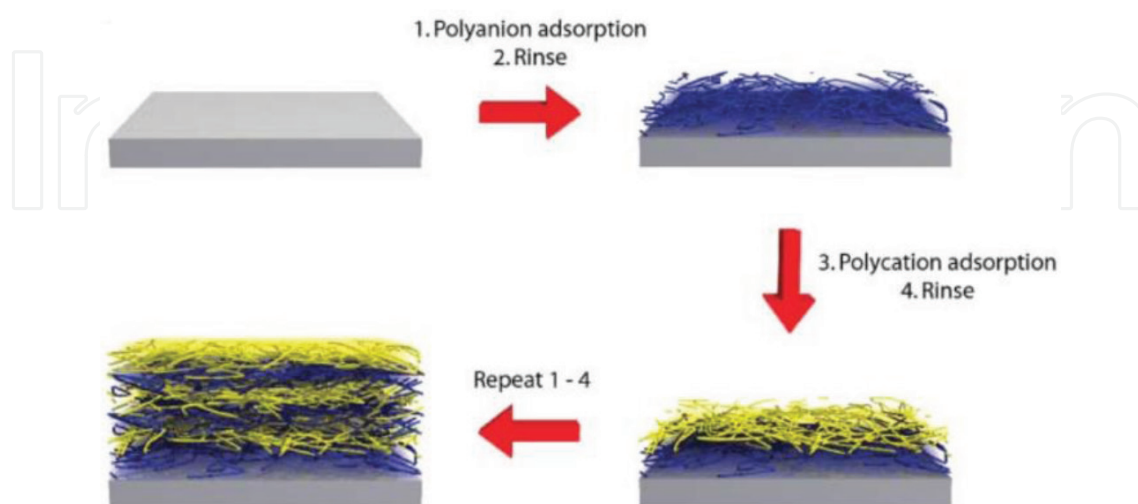


Figure 7. LbL assembly of polyelectrolytes on planar substrates. Copyright 2007 Royal Society of Chemistry.

followed by thorough rinsing. Reversal of the surface charge then facilitates further adsorption steps. The process is continued until the desired layer number (or thickness) is achieved.

The technique is still expanding its potential because of its versatility for the fabrication of ordered multilayers. Molecular self-assembly of macromolecules and nanoreactors is controlled by the interplay of intra- and intermolecular as well as interfacial interactions. Through tuning the intra- and intermolecular interactions, films and layers with varied surface properties could be obtained.

Serhiy et al. reported an LbL thin film **8** for ammonia sensing where porphyrin was adopted as a responsive element (**Figure 8**) [35]. It showed that the sensing sensitivity was greatly dependent on the film thicknesses. Upon ammonia exposure, the optical spectrum of film **8** obtained by LbL assembling for 15 cycles had a response time less than 30 s and it showed a linear relation with ammonia concentrations (0–100 ppm).

1.2.4. Electrospinning films

Ultrathin films, such as nanofiber films with different structures and functions, have been developed for environmental applications in recent years. Electrospinning was an easy but versatile method for various polymers to fabricate ultrathin films. Differing from normal fibers, the electrospun ultrathin fibers show nanoscale diameters, high lengths, and large surface area to volume ratios [36]. By controlling the processing parameters, different fibers could be obtained with various morphologies, such as core-shell, hollow, and porous structures [37, 38]. Generally, the sensitivity of a sensor will increase with a growing surface area

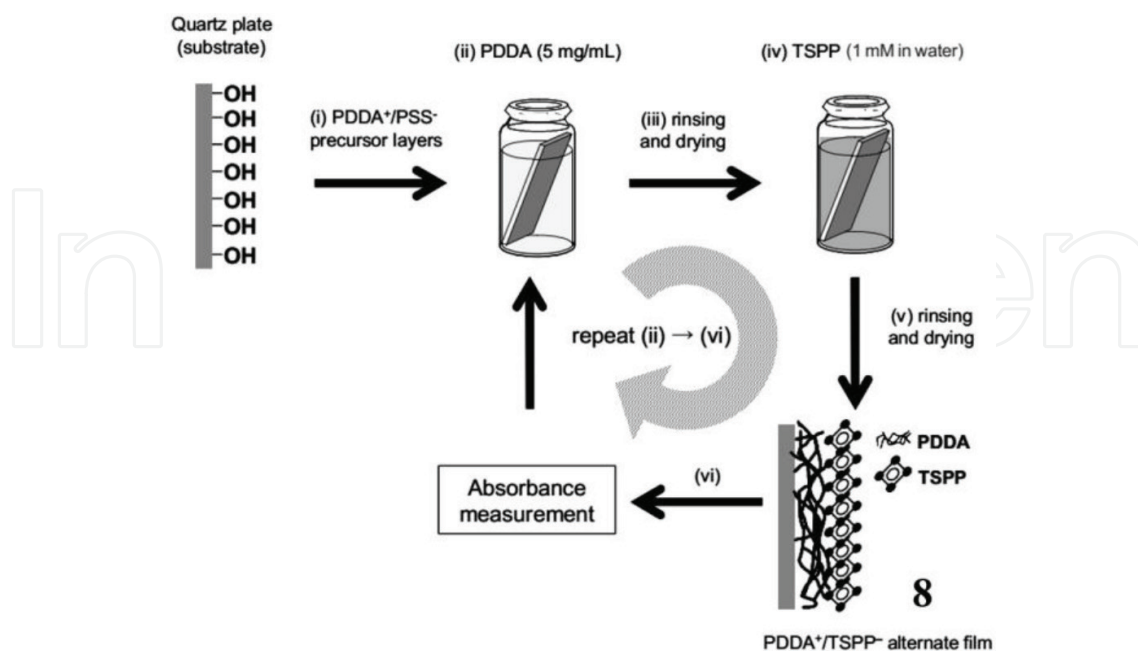


Figure 8. Preparation of film **8** via electrostatic LbL adsorption. Copyright 2006 Collegium Basilea & AMSI.

per unit mass, due to the detection carried out on the sensor surface [39]. Therefore, the large surface area to volume ratio and good interconnectivity make electrospun ultrathin fibers highly attractive for sensor applications. It is worth noting that a porous nanostructured fiber can be generated directly by controlling phase separation during electrospinning. The enhanced surface to volume ratio of the porous nanofibers could improve the sensitivity of the sensors.

There are two main classifications of fabrication processes of ultrathin fiber sensors. One is to incorporate sensing substances onto the outer surface of electrospun fibers. Sensors fabricated by this method usually have higher sensitivity but are unstable in external environment. Lee et al. reported a dots-on-fibers (DoF) hybrid nanostructure **9** via simple electrospinning and subsequent immobilization processes (**Figure 9**) [40]. The conjugated polymer dots (CPdots) was immobilized on the surface of poly(vinyl alcohol) (PVA)-silica nanofibers. The CPdots and amine-functionalized electrospun PVA-silica nanofibers interacted via electrostatic interaction.

Another strategy is to fabricate nanofiber sensors directly by adding sensing elements into the spinning solution. Ding et al. reported an approach for colorimetric quantitative detection of Pb^{2+} by embedding newly synthesized polydiacetylenes (PDA) into the electrospun polyacrylonitrile nanofibrous membrane (PAN NFM, **Figure 10**) [41]. Compared with the casting film-based PAN NFM, the electrospun film **10** displayed much higher sensitivity. Moreover, the morphology and porous structure of **10** could be further regulated by tuning the concentration of PAN, which displayed profound influence on sensing performance.

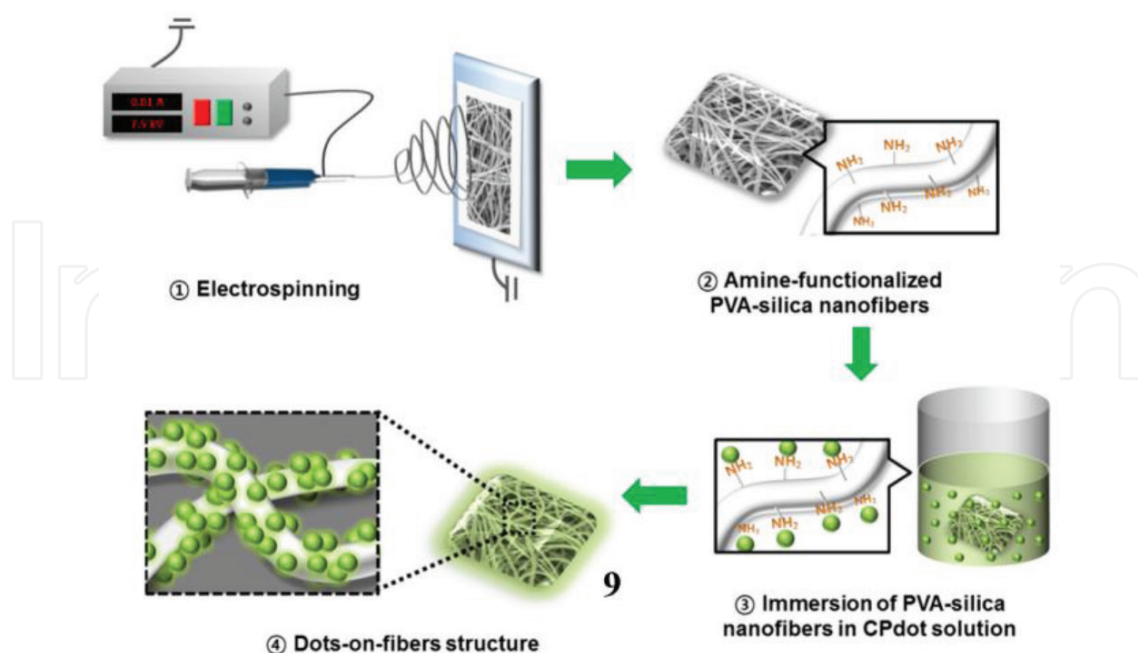


Figure 9. Preparation of DoF structure **9** by electrospinning and subsequently surface modification of the obtained fiber. Copyright 2014 American Chemical Society.

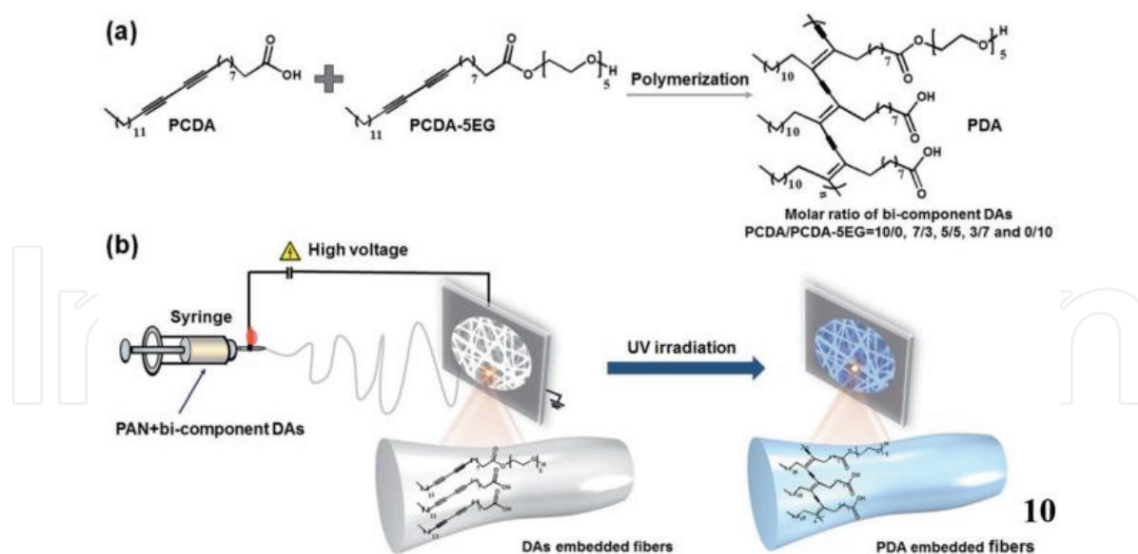


Figure 10. (a) Preparation of PDA polymers. (b) Schematic representation of the preparation of the PDA embedded film 10. Copyright 2014 Royal Society of Chemistry.

2. FLL for the detection of environmental pollutants

2.1. Gaseous pollutant detection

2.1.1. Carbon dioxide (CO_2) detection

Carbon dioxide is a major public concern with widespread discussion because of its role in global greenhouse warming. Moreover, CO_2 is also quite critical to the modern agricultural, food, environmental, oil, and chemical industries. However, it is dangerous for living beings to stay at high concentration levels of CO_2 [42]. Therefore, the importance and prevalence of such a gas (CO_2) provides an incentive for development of new methods that can be used for the rapid and selective detection and monitoring of this relatively inert gas both in gaseous and liquid phases. Some traditional detection methods, such as electrochemical and infrared spectroscopic techniques, are usually employed for CO_2 sensing and detection; however, these methods are believed to be expensive and time consuming. Hence, the development of chemosensors for determining the concentration level of CO_2 is of great interest.

The use of pH indicators is one strategy in the construction of fluorescent sensors for CO_2 detection. The most famous pH indicator used for sensing CO_2 is 1-hydroxypyrene-3,6,8-trisulfonate (HPTS, **11**), as shown in **Figure 11a**. For instance, Sampathkumaran et al. reported the development of a sol-gel fluorescent sensor for detecting CO_2 with a detection limit below the amount of CO_2 in the atmosphere (ca. 387 ppm) (**Figure 11b**) [43]. In their work, a sol-gel fluorescent sensor was modified into silica-doped matrix with **11** by spin coating on glass slides. The fluorescent intensity of this indicator (513 nm) was quenched by CO_2 as a result of protonation of the anionic form.

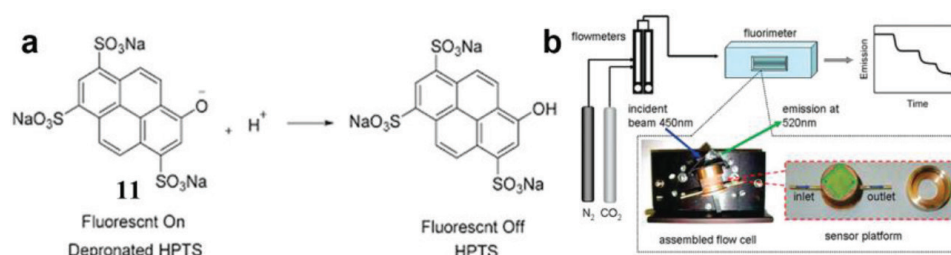


Figure 11. (a) Structures of pH indicator **11** as a CO₂ sensor. (b) Schematic diagram of the sensing system based on **11**-doped polymeric film. Copyright 2010 American Chemical Society.

Another strategy was developed based on chemical reaction between amine and CO₂. CO₂ is a weak electrophile that can react with an active basic amine to form corresponding carbamate salt and ammonium salt. Sijbesma et al. investigated the reaction between CO₂ and optically pure chiral diamines **12** ((R,R)-**12** or (S,S)-**12**), **Figure 12** [44]. This strategy for monitoring CO₂ is also based on the reversible carbamate formation-decomposition mechanism. The corresponding diamine/diol complex was utilized for reacting with CO₂ and results in apparent color change as well as in a helical twisting power. Moreover, this sensing platform showed a continuous reversible response for CO₂ monitoring based on the equilibrium complexation of **12** with CO₂.

2.1.2. Ammonia gas detection

Ammonia (NH₃) is widely employed in industrial and agricultural systems such as refrigeration, stock farming, fertilizer production, and food processing [45]. In addition to its broad applications, ammonia is also toxic, irritating, and corrosive to human skin, eyes, and respiratory system [46]. Recently, fluorescent sensors for ammonia detection have shown great promise with their low cost, easy use, and high sensitivity.

Gu and Huang reported the polyaniline **13** deposited filter paper as a reversible colorimetric sensor for gaseous ammonia (**Figure 13**) [47]. In this research, the authors utilized conducting

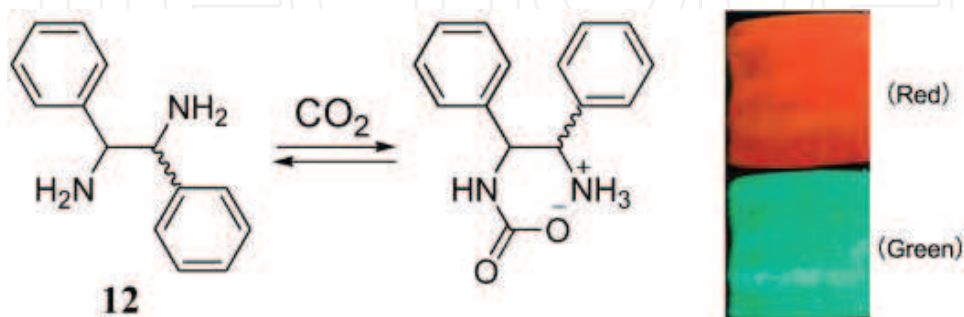


Figure 12. (Left) Structures of CO₂ responsive chiral dopant **12**. (Right) Cholesteric liquid crystals (CLC) film before (top) and after (bottom) exposure to CO₂ for 1 hour. Copyright 2010 American Chemical Society.

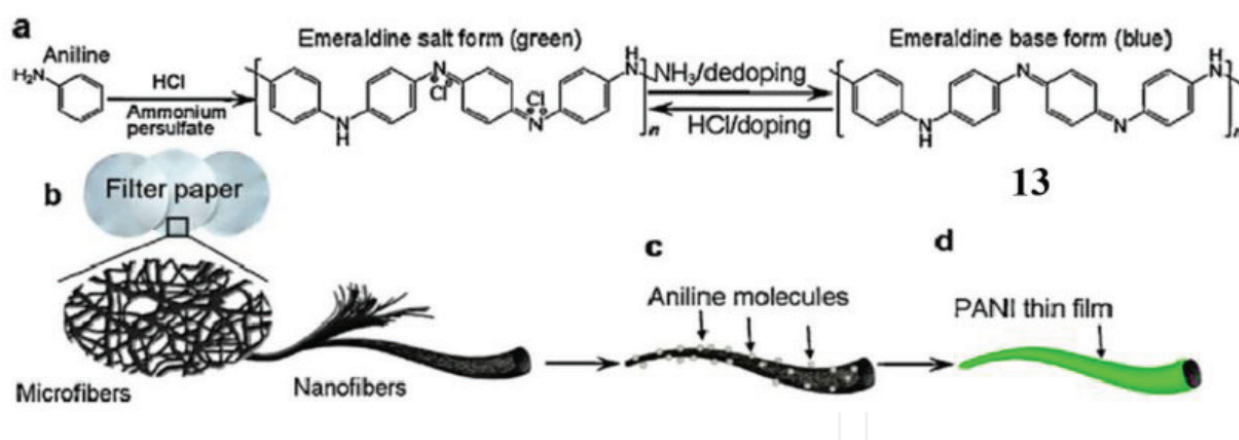


Figure 13. Scheme for the color transition of **13** (a) and the fabrication process of the **13**-deposited filter paper (b–d). Copyright 2013 Elsevier B.V. All rights reserved.

polymer, which has various advantages, such as tunable conductivity, a reversible doping/dedoping mechanism, and high affinity for ammonia. Nanometer-thick films were uniformly coated on cellulose nanofiber via in situ polymerization of anilines. Upon protonation by hydrochloride, the emeraldine salt type of **13** displayed green color, while the emeraldine base underwent deprotonation upon the addition of ammonia, resulting in color change into blue. The detection limits of this film by the naked eye were 100 ppm for the gaseous state ammonia under nitrogen atmosphere and 10 ppm for the evaporated ammonia aqueous solution. Furthermore, these color transitions were fully reversible.

Colored sensing films have slight color variations especially under low concentrations of ammonia, which are not easily perceived by visual inspection. Yin et al. reported a flexible naked eye ammonia sensor mat **14** by blending a hydrophobic cyanine dye into polylactic acid (PLA) porous fibers [48]. Upon exposure to ammonia vapor, the sensing mat experienced perceivable color change from white to blue. The fibrous mat **14** exhibited high selectivity for ammonia gas with a detection limit of 3.3 ppm. The white to blue color changing process was attributed to ionization-induced deaggregation of cyanine dyes (**Figure 14**).

2.1.3. Hydrogen chloride gas (HCl) detection

Sensitive detection and monitoring of HCl gas have attracted a lot of attention [49]. HCl is mainly released in the mass production of halogenated polymers. Therefore, it is of great importance to sense and regulate HCl concentration in the adsorbing towers of these factories, which benefits the emission monitoring and air quality control.

As shown in **Figure 15**, Wu and coworkers reported an HCl gas sensor **15** with rapid response-recovery manner, which was fabricated from the nanofibrous membrane of porphyrinated polyimide (PPI) [50]. Exposing **15** to HCl gas induced absorption change within 10 s and color varied in response to different concentrations of HCl gas. Apparent binding affinity constant calculated from surface plasmon resonance (SPR) analysis is found to be $(1.05 \pm 0.23) \times 10^4 \text{ L mol}^{-1}$. The superior thermal stability of PPI makes this nanofibrous membrane sensor promising for monitoring HCl gas emission in incinerators for burning domestic, clinical, or industrial wastes.

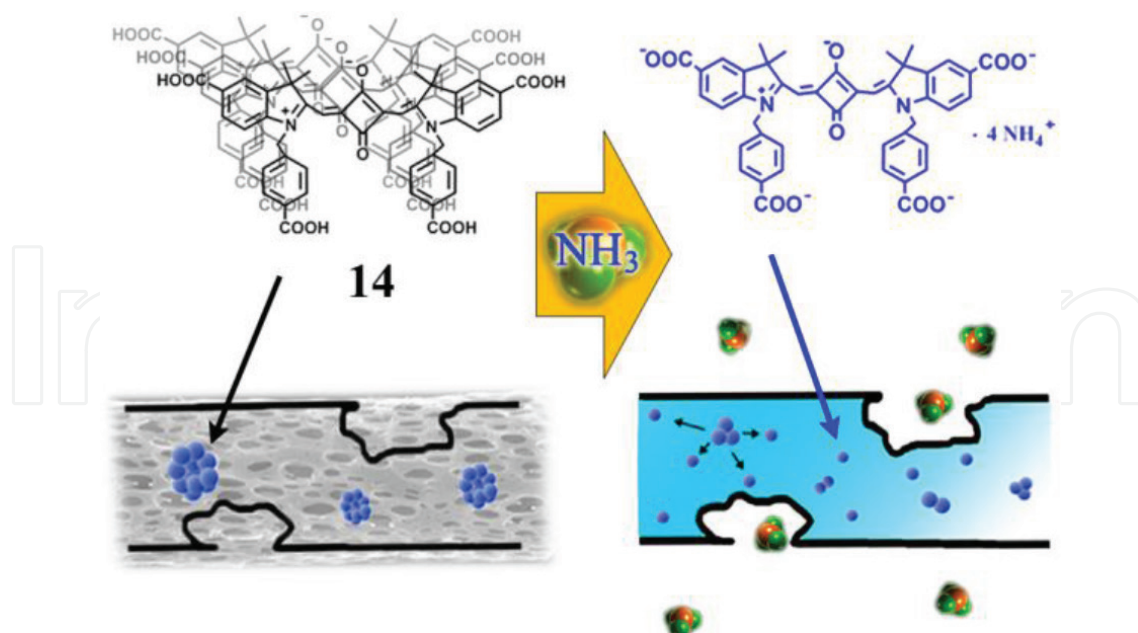


Figure 14. Structure of the sensor **14** and proposed sensing mechanism of **14**-doped electrospun fiber. Copyright 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

2.1.4. Volatile organic compound (VOC) detection

The detection of volatile organic compounds is an important aspect considering that VOCs are continuously released into the environment by different sources like industrial processes, transportation, agriculture, etc. [51]. These VOCs not only cause environmental pollution but also directly affect human health. For example, alcohols and aromatic hydrocarbons

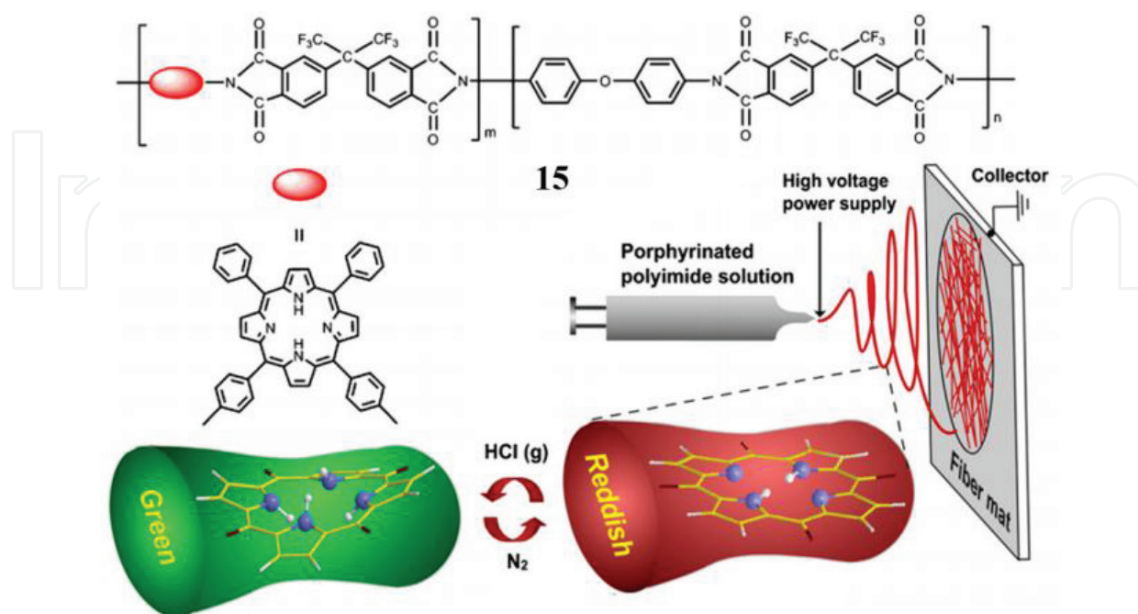


Figure 15. Molecular structure of **15** and the schematic illustration for the fluorescent detection of HCl gas. Copyright 2010 Elsevier B.V. All rights reserved.

are potentially hazardous to human health due to their capabilities to stimulate the mucous membranes and upper respiratory tracts [52]. Various detection methods have been proposed based on changes in electrochemical, conducting, and chromism properties of the corresponding sensor matrices. Colorimetric sensor systems are of particular interest thanks to their effectiveness and simplicity.

Formaldehyde could be slowly released from many building materials such as paints, adhesives, wallboards, and ceiling tiles, which irritates the mucous membranes and can make a person irritated and uncomfortable. The reaction of primary amine with aldehyde is often utilized to detect formaldehyde. Suslick and coworkers utilized simple pH indicators to detect the change in basicity as a simple colorimetric system for gaseous formaldehyde (**Figure 16**) [53]. Six different pH indicators, such as methyl red, bromocresol purple, 4-nitrophenol, alizarin, nitrazine yellow, and bromoxylene blue, were introduced into a poly(ethylene glycol) (PEG) polymer containing five different amounts (0.24, 0.48, 0.58, 0.82, and 1.03 wt%) of PEG with amine termination. This polymer film **16** displayed distinct colorimetric changes with different concentrations of formaldehyde.

Synthetic amines are produced in millions of tons each year and have broad applications in agricultural, pharmaceutical, and food industries. The excess of organic amines in air would seriously damage the ecological environment and pose severe threats to human health. Selective detection of trace amines in the vapor phase has attracted intense attention because of the increasing concerns regarding air pollution monitoring, quality control of food, and even medical diagnosis. Lin and coworkers reported an AIE dye **17**-based fluorescence sensing film for alkylamines (**Figure 17**) [54]. The fluorescence intensity of **17** enhanced by 30- to 50-fold toward ammonia, hydrazine, and alkyl amines (benzylamine, EtNH_2 , Et_2NH , NMe_3 , Et_3N). The light-up ratios (I/I_0) indicate that these amine vapors can efficiently cleave the *O*-acetyl bond to generate highly emissive product through aminolysis reaction. However, for aromatic amines (aniline, 2-methylaniline), biogenic amines such as putrescine, cadaverine, histamine, and organic solvent vapors such as hexane, CH_2Cl_2 , EtOAc, THF, MeCN, MeOH, and EtOH, almost no light-up response was observed.

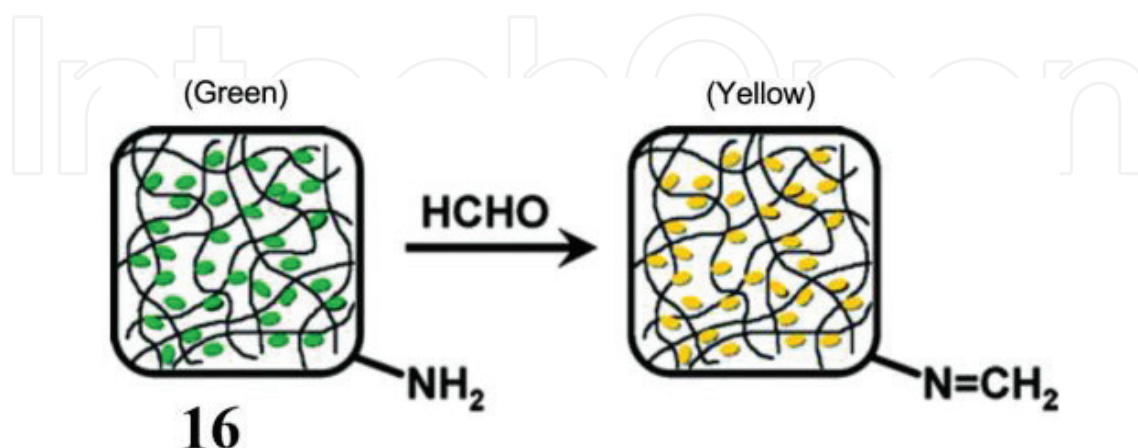


Figure 16. Schematic presentation of sensing film **16** for formaldehyde. Copyright 2010 American Chemical Society.

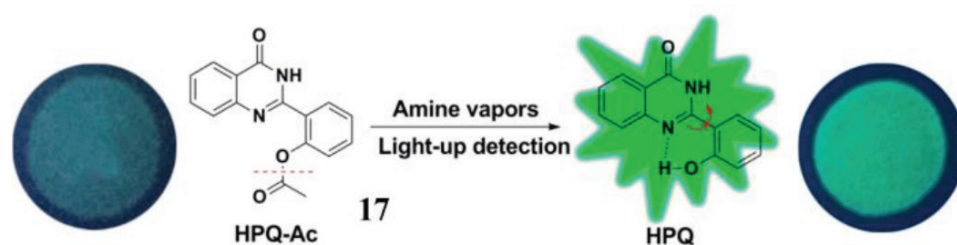


Figure 17. Chemical structure of **17** and its light-up response to amine vapors. Copyright 2016 American Chemical Society.

2.2. Metal ion detection

During the last decades, increased contributions of contaminants caused drastic changes in ecosystems. Soil and water pollution with metals especially heavy metals is very frequently encountered. Metals are not biodegradable, and therefore they remain in ecological systems and in the food chain indefinitely, exposing top-level predators to very high levels of pollution. These interactions metals have toxicological and carcinogenic effects such as those affecting the central nervous system (Hg^{2+} , Pb^{2+} , As^{2+}); the kidneys or liver (Cu^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+}); or skin, bones, or teeth (Ni^{2+} , Cu^{2+} , Cd^{2+} , Cr^{2+}) [55]. Therefore, World Health Organization (WHO) and Environmental Protection Agency (EPA) have strictly defined the concentration limits of metal ions that are allowed in the drinking water. Especially, lead, cadmium, and mercury ions are banned in electrical and electronic equipment by the European Union's Restriction on Hazardous Substances (RoHS) [56]. As is well known, standard techniques for trace heavy-metal analysis (even in the ppt and ppq range) require sophisticated analytical techniques such as atomic absorption spectroscopy (AAS), inductively coupled plasma-mass spectrometry (ICPMS), mass spectrometry (MS), X-ray fluorescence spectroscopy (R-FS), and potentiometric methods and specialized personnel to carry out the operational procedures [55]. Efforts are ongoing to prepare rapid and inexpensive techniques for heavy-metal detection. Here, optical detections for heavy-metal ions based on fluorescent films are reviewed.

2.2.1. Mercury ion (Hg^{2+}) detection

Mercury is widespread in air, water, and soil and is notoriously known for its high toxicity to human beings such as severe damage to the central nervous system. Moreover, accumulation of mercury in human body could lead to various kinds of cognitive and motor disorders as well as Minamata disease [57]. Many sources are to blame for the generation of mercury, for example, coal plants, gold production, measuring instrument, and mercury lamps [58]. Mercury is mainly uptaken by human beings through daily diet such as fish, and it is vital that considerable efforts should focus on the development and evolution of sensitive and selective detection methods.

Yin et al. reported a highly sensitive and selective fluorescent nanofibrous membrane **18** for the detection of mercuric ions (II) (**Figure 18**) [59]. **18** was prepared via electrospinning and

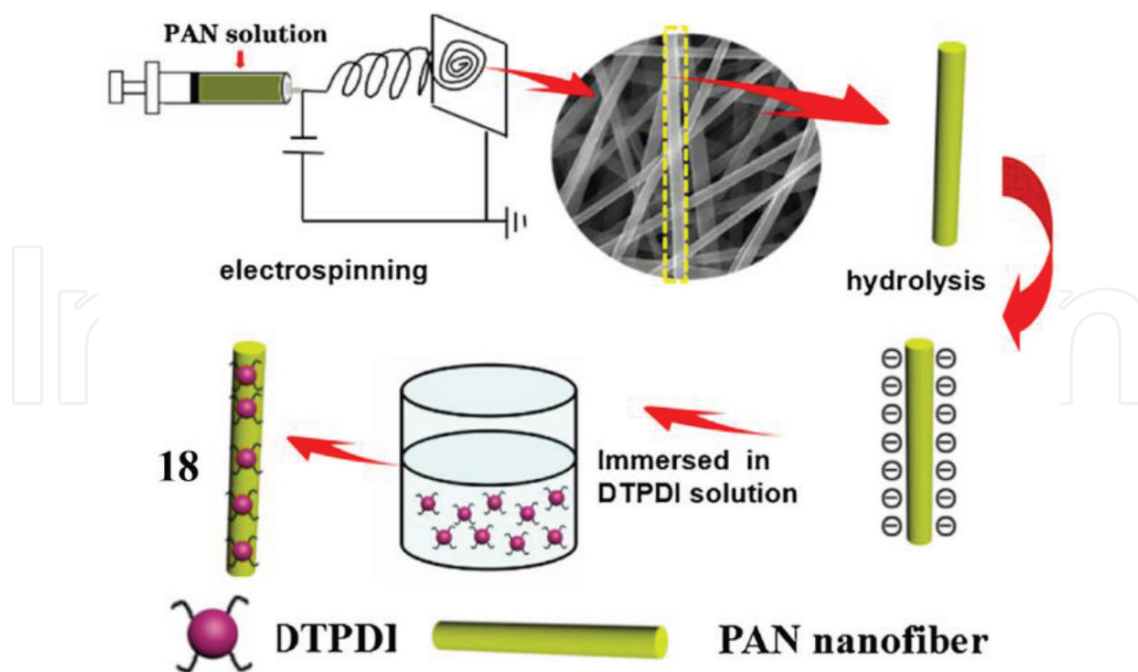


Figure 18. Schematic illustration for the fabrication sensing film **18** for Hg²⁺. Copyright 2017 Elsevier B.V. All rights reserved.

subsequent immobilization. In this process, fluorescent chemosensor dithioacetal-modified perylene-3,4,9,10-tetracarboxylic diimide (DTPDI) was introduced on the surface of PAN nanofibers with high stability under mechanical force by electrostatic interaction. DTPDI could detach from PAN nanofibers due to the hydrolysis of dithioacetals in the presence of Hg²⁺ and form an oil-soluble fluorescence dye AL. According to the linear correlation between AL and Hg²⁺, the obtained **18** could be employed for the detection of Hg²⁺. The limit of detection for Hg²⁺ can reach as low as 1 ppb. In addition, the strong fluorescence of **18** still can be observed even after the repeated use for seven times. **18** can be developed as a rapid, portable, and stable sensor for the detection of Hg²⁺.

2.2.2. Lead ion (Pb²⁺) detection

As an abundant but toxic metal, lead is often left in the environment due to its application in batteries, gasoline, pigments, etc. [60]. Lead pollution causes long-term damage to both human health and the environment, as most of the mined lead, 300 million tons to date, is still going back to soil and groundwater finally. Trace amounts of lead may cause neurological, reproductive, cardiovascular, and developmental disorders. Particularly, lead poisoning will introduce serious problems in children including slow motor responses, decreased IQs, and hypertension.

Kim et al. reported a rhodamine-based chemosensor **19** for the selective fluorescent sensing of Pb²⁺ (**Figure 19**) [61]. **19** was synthesized and self-assembled onto glass surfaces as a film sensor. The immobilized chemosensor showed a fluorescent response that was turned-on with Pb²⁺ in CH₃CN, selectively over various metal ions. The selective fluorescent change of sensor

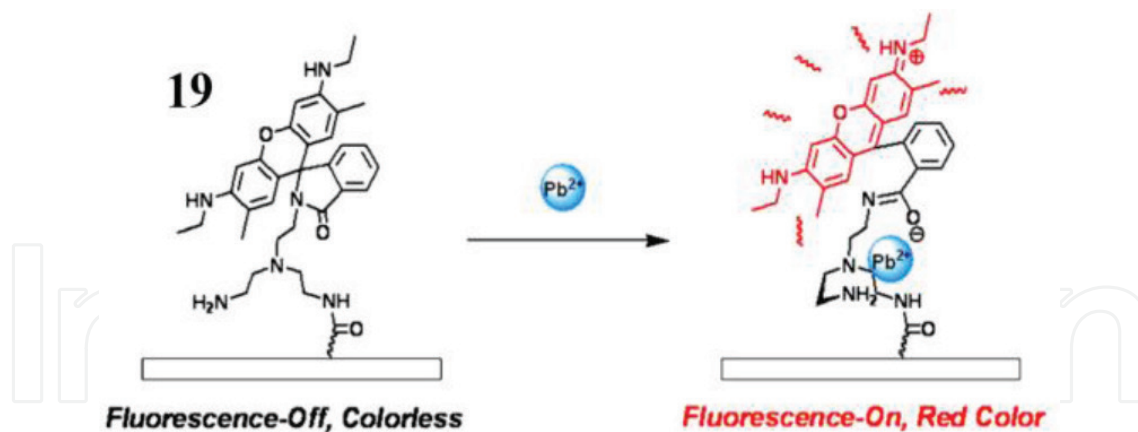


Figure 19. Rhodamine-based chemosensor **19** and its fluorescent “turn-on” response for Pb^{2+} . Copyright 2011 Elsevier B.V. All rights reserved.

was 1223 ± 166 counts only for Pb^{2+} over other cations. The detection limit of Pb^{2+} ($S/N = 3$) was approximately 10^{-4} M. The Pb^{2+} selective fluorescent switch of the immobilized chemosensor was also reversible, allowing for repeated use for Pb^{2+} detection.

2.2.3. Cadmium ion (Cd^{2+}) detection

Cadmium is a kind of heavy metal with severe toxicity and carcinogenicity. It is commonly seen in electric batteries, pigments in plastics, electroplated steel, and so on [62]. Human being tends to uptake cadmium mainly through smoking and daily diet. Exposure to high concentration of cadmium would result in increased risk in cardiovascular diseases and cancer, and it may also cause damage to liver and kidneys [63].

Wei et al. reported a fluorescence layered double hydroxide (LDH) ultrathin films **20** fabricated by alternate assembly of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS) and ZnAl LDH nanosheets on quartz substrates using the LbL deposition technique (**Figure 20**) [64]. **20** performed as a good fluorescence chemosensors for Cd^{2+} . The fluorescent sensor with

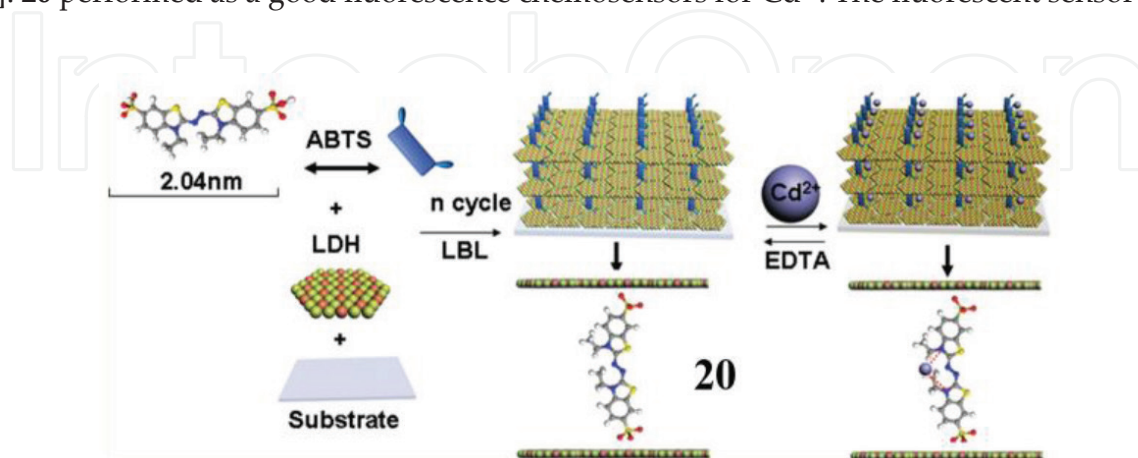


Figure 20. Schematic representation of the measurement-regeneration cycle of **20**. Copyright 2011 American Chemical Society.

20 bilayers showed a low detection limit of 9.5 nM for Cd^{2+} , good selectivity toward Cd^{2+} from Zn^{2+} at pH 6.5 to 7.5 and excellent stability. The regeneration of **20** can be achieved during a repeat procedure by using ethylenediamine tetraacetic (EDTA).

3. Conclusion

This chapter reports the preparation of nanoscaled FFL and the detection of environmental pollutants. Several sensing strategies are brought up based on the different dyes. Nanoscaled FFL act as a promising tool for hazardous pollutant detection, including gaseous pollutants (such as CO_2 , NH_3 , HCl gas, and VOCs) and metal ions (such as Hg^{2+} , Pb^{2+} , Cd^{2+}). However, although numerous chemosensors for gases/ions have been widely developed and applied, a big challenge remains to construct those that display high selectivities, sensitivities, and reusabilities.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21574009 and 51521062), Beijing collaborative innovative research center for cardiovascular diseases, and the Higher Education and High-quality and World-class Universities (PY201605).

Author details

Meizhen Yin* and Chendong Ji

*Address all correspondence to: yinmz@mail.buct.edu.cn

State Key Laboratory of Chemical Resource Engineering, Beijing Laboratory of Biomedical Materials, Beijing University of Chemical Technology, Beijing, China

References

- [1] Lubchenco J. Entering the century of the environment: a new social contract for science. *Science* 1998; **279**: 491–497.
- [2] Ji X, Banks CE, Silvester DS, et al. Electrochemical ammonia gas sensing in nonaqueous systems: a comparison of propylene carbonate with room temperature ionic liquids. *Electroanalysis* 2007; **19**: 2194–2201.
- [3] Moujahid W, Eichelmann-Daly P, Strutwolf J, et al. Microelectrochemical systems on silicon chips for the detection of pollutants in seawater. *Electroanalysis* 2011; **23**: 147–155.

- [4] Balakumar V, Prakash P, Muthupandi K, et al. Nanosilver for selective and sensitive sensing of saturnism. *Sens. Actuators B. Chem.* 2017; **241**: 814–820.
- [5] Wu J, Kwon B, Liu W, et al. Chromogenic/fluorogenic ensemble chemosensing systems. *Chem. Rev.* 2015; **115**: 7893–7943.
- [6] Sinkeldam RW, Greco NJ, Tor Y. Fluorescent analogs of biomolecular building blocks: design, properties, and applications. *Chem. Rev.* 2010; **110**: 2579–2619.
- [7] Chen M, Yin M. Design and development of fluorescent nanostructures for bioimaging. *Prog. Polym. Sci.* 2014; **39**: 365–395.
- [8] Perreault F, de Faria AF, Elimelech M. Environmental applications of graphene-based nanomaterials. *Chem. Soc. Rev.* 2015; **44**: 5861–5896.
- [9] Fölling J, Bossi M, Bock H, et al. Fluorescence nanoscopy by ground-state depletion and single-molecule return. *Nat. methods* 2008; **5**: 943–945.
- [10] Lü B, You S, Li P, et al. Kinetically trapped supramolecular assembly of perylene dianhydride derivative in methanol: optical spectra, morphology, and mechanisms. *Chem. Eur. J.* 2016; **22**: 1–6.
- [11] De Silva AP, Gunaratne HQN, Gunnlaugsson T, et al. Signaling recognition events with fluorescent sensors and switches. *Chem. Rev.* 1997; **97**: 1515–1566.
- [12] Martínez-Manez R, Sancenon F. Fluorogenic and chromogenic chemosensors and reagents for anions. *Chem. Rev.* 2003; **103**: 4419–4476.
- [13] Sapsford KE, Berti L, Medintz IL. Materials for fluorescence resonance energy transfer analysis: beyond traditional donor–acceptor combinations. *Angew. Chem. Int. Ed.* 2006; **45**: 4562–4589.
- [14] Zhang J, Liu K, Müllen K, et al. Self-assemblies of amphiphilic homopolymers: synthesis, morphology studies and biomedical applications. *Chem. Commun.* 2015; **51**: 11541–11555.
- [15] Hong Y, Lam JWY, Tang BZ. Aggregation-induced emission: phenomenon, mechanism and applications. *Chem. Commun.* 2009; **29**: 4332–4353.
- [16] Herman P, Murtaza Z, Lakowicz JR. Sensing of carbon dioxide by a decrease in photo-induced electron transfer quenching. *Anal. Biochem.* 1999; **272**: 87–93.
- [17] Lee SH, Kim SK, Bok JH, et al. Calix[4]crown in dual sensing functions with FRET. *Tetrahedron Lett.* 2005; **46**: 8163–8167.
- [18] Liu K, Xu Z, Yin M, et al. A multifunctional perylene diimide derivative (DTPDI) can be used as a recyclable specific Hg²⁺ ion sensor and an efficient DNA delivery carrier. *J. Mater. Chem. B.* 2014; **2**: 2093–2096.
- [19] Liu Y, Tang Y, Barashkov NN, et al. Fluorescent chemosensor for detection and quantitation of carbon dioxide gas. *J. Am. Chem. Soc.* 2010; **132**: 13951–13953.

- [20] Yagai S, Seki T, Karatsu T, et al. Transformation from H-to J-aggregated perylene bisimide dyes by complexation with cyanurates. *Angew. Chem. Int. Ed.* 2008; **47**: 3367–3371.
- [21] Li J, Lv B, Yan D, et al. Tunable self-assembled micro/nanostructures of carboxyl-functionalized squarylium cyanine for ammonia sensing. *Adv. Funct. Mater.* 2015; **25**: 7442–7449.
- [22] Zhang Q, Uchaker E, Candelaria SL, et al. Nanomaterials for energy conversion and storage. *Chem. Soc. Rev.* 2013; **42**: 3127–3171.
- [23] Innocenzi P, Malfatti L. Mesoporous thin films: properties and applications. *Chem. Soc. Rev.* 2013; **42**: 4198–4216.
- [24] Jayasekara R, Harding I, Bowater I, et al. Preparation, surface modification and characterisation of solution cast starch PVA blended films. *Polym. Test.* 2004; **23**: 17–27.
- [25] Sasaki DY, Singh S, Cox JD, et al. Fluorescence detection of nitrogen dioxide with perylene/PMMA thin films. *Sens. Actuators B.* 2001; **72**: 51–55.
- [26] Liu Y, Wang KR, Guo DS, et al. Supramolecular assembly of perylene bisimide with β -cyclodextrin grafts as a solid-state fluorescence sensor for vapor detection. *Adv. Funct. Mater.* 2009; **19**: 2230.
- [27] Jiang BP, Guo DS, Liu Y. Self-assembly of amphiphilic perylene-cyclodextrin conjugate and vapor sensing for organic amines. *The J. Org. Chem.* 2010; **75**: 7258–7264.
- [28] Remunan-Lopez C, Bodmeier R. Mechanical, water uptake and permeability properties of crosslinked chitosan glutamate and alginate films. *J. Org. Chem.* 1997; **44**: 215–225.
- [29] Yin M, Ye Y, Sun M, et al. Facile one-pot synthesis of a polyvinylpyrrolidone-based self-crosslinked fluorescent film. *Macromol. Rapid Commun.* 2013; **34**: 616–620.
- [30] Sun M, He Y, Ye Y, et al. Nucleophilic substitution of tetrachloroperylene diimide in fluorescent polyvinylpyrrolidone film. *Macromol. Chem. Phys.* 2014; **215**: 493–498.
- [31] Sun M, He Y, Yang W, et al. A fluorescent perylene-assembled polyvinylpyrrolidone film: synthesis, morphology and nanostructure. *Soft Matter*, 2014; **10**: 3426–3431.
- [32] Iler RK. Multilayers of colloidal particles. *J. Colloid Interface Sci.* 1966; **21**: 569–594.
- [33] Decher G, Hong JD. Buildup of ultrathin multilayer films by a self-assembly process, 1 consecutive adsorption of anionic and cationic bipolar amphiphiles on charged surfaces. *Macromol. Symp.* 1991; **46**: 321–327.
- [34] Quinn JF, Johnston APR, Such GK, et al. Next generation, sequentially assembled ultrathin films: beyond electrostatics. *Chem. Soc. Rev.* 2007; **36**: 707–718.
- [35] Korposh SO, Takahara N, Ramsden JJ, et al. Nano-assembled thin film gas sensors. 1. Ammonia detection by a porphyrin-based multilayer film. *J. Biol. Phys. Chem.* 2006; **6**: 125–132.

- [36] Ding B, Wang M, Wang X, et al. Electrospun nanomaterials for ultrasensitive sensors. *Mater. Today*, 2010; **13**: 16–27.
- [37] Zhao Y, Cao X, Jiang L. Bio-mimic multichannel microtubes by a facile method. *J. Am. Chem. Soc.* 2007; **129**: 764–765.
- [38] Li D, Xia Y. Direct fabrication of composite and ceramic hollow nanofibers by electrospinning. *Nano Lett.* 2004; **4**: 933–938.
- [39] Wang X, Drew C, Lee SH, et al. Electrospun nanofibrous membranes for highly sensitive optical sensors. *Nano Lett.* 2002; **2**: 1273–1275.
- [40] Jo S, Kim J, Noh J, et al. Conjugated polymer dots-on-electrospun fibers as a fluorescent nanofibrous sensor for nerve gas stimulant. *ACS Appl. Mater. Interfaces* 2014; **6**: 22884–22893.
- [41] Li Y, Wang L, Yin X, et al. Colorimetric strips for visual lead ion recognition utilizing polydiacetylene embedded nanofibers. *J. Mater. Chem. A.* 2014; **2**: 18304–18312.
- [42] Tian T, Chen X, Li H, et al. Amidine-based fluorescent chemosensor with high applicability for detection of CO₂: a facile way to “see” CO₂. *Analyst* 2013, **138**: 991–994.
- [43] Dansby-Sparks RN, Jin J, Mechery SJ, Sampathkumaran U. et al. Fluorescent-dye-doped sol-gel sensor for highly sensitive carbon dioxide gas detection below atmospheric concentrations. *Anal. Chem.* 2009; **82**: 593–600.
- [44] Han Y, Pacheco K, Bastiaansen CWM, Broer DJ and Sijbesma RP. Optical monitoring of gases with cholesteric liquid crystals. *J. Am. Chem. Soc.* 2010; **132**: 2961–2967.
- [45] Timmer B, Olthuis W, Van Den Berg A. Ammonia sensors and their applications—a review. *Sens. Actuators B.* 2005; **107**: 666–677.
- [46] Max A. Ammonia: Principles and Industrial Practice. Vch Verlagsgesellschaft Mbh, 1999.
- [47] Gu Y, Huang J. Colorimetric detection of gaseous ammonia by polyaniline nanocoating of natural cellulose substances. *J. Colloids Surf. A: Physicochem. Eng. Aspects* 2013; **433**: 166–172.
- [48] Ji C, Ma L, Yin M, et al. A cyanine dye encapsulated porous fibrous mat for naked-eye ammonia sensing. *Chem. Asian J.* 2016; **11**: 2316–2321.
- [49] Matsuguchi M, Kadowaki Y. Poly (acrylamide) derivatives for QCM-based HCl gas sensor applications. *Sens. Actuators B.* 2008; **130**: 842–847.
- [50] Lv YY, Wu J, Xu ZK. Colorimetric and fluorescent sensor constructing from the nanofibrous membrane of porphyrinated polyimide for the detection of hydrogen chloride gas. *Sens. Actuators B.* 2010; **148**: 233–239.
- [51] Adgate JL, Goldstein BD, McKenzie LM. Potential public health hazards, exposures and health effects from unconventional natural gas development. *Environ. Sci. Technol.* 2014; **48**: 8307–8320.

- [52] Room R, Babor T, Rehm J. Alcohol and public health. *Lancet* 2005; **365**: 519–530.
- [53] Feng L, Musto CJ, Suslick KS. A simple and highly sensitive colorimetric detection method for gaseous formaldehyde. *J. Am. Chem. Soc.* 2010; **132**: 4046–4047.
- [54] Gao M, Li S, Lin Y, et al. Fluorescent light-up detection of amine vapors based on aggregation-induced emission. *ACS Sens.* 2015; **1**: 179–184.
- [55] Aragay G, Pons J, Merkoçi A. Recent trends in macro-, micro-, and nanomaterial-based tools and strategies for heavy-metal detection. *Chem. Rev.* 2011; **111**: 3433–3458.
- [56] Kim HN, Ren WX, Kim JS, et al. Fluorescent and colorimetric sensors for detection of lead, cadmium, and mercury ions. *Chem. Soc. Rev.* 2012, **41**: 3210–3244.
- [57] Carvalho CML, Chew EH, Hashemy SI, et al. Inhibition of the human thioredoxin system a molecular mechanism of mercury toxicity. *J. Biol. Chem.* 2008; **283**: 11913–11923.
- [58] Di Natale F, Lancia A, Molino A, et al. Capture of mercury ions by natural and industrial materials. *J. Hazard. Mater.* 2006; **132**: 220–225.
- [59] Ma L, Liu K, Yin M, et al. Fluorescent nanofibrous membrane (FNFM) for the detection of mercuric ion (II) with high sensitivity and selectivity. *Sens. Actuators B.* 2017; **238**: 120–127.
- [60] Flegal AR, Smith DR. Current needs for increased accuracy and precision in measurements of low levels of lead in blood. *Environ. Res.* 1992; **58**: 125–133.
- [61] Ju H, Lee MH, Kim J, et al. Rhodamine-based chemosensing monolayers on glass as a facile fluorescent “turn-on” sensing film for selective detection of Pb^{2+} . *Talanta* 2011; **83**: 1359–1363.
- [62] Nordberg GF, Herber RFM, Alessio L. *Cadmium in the Human Environment*, Oxford University Press, Oxford, UK, 1992.
- [63] McFarland CN, Bendell-Young LI, Guglielmo C, et al. Kidney, liver and bone cadmium content in the Western Sandpiper in relation to migration. *J. Environ. Monit.* 2002; **4**: 791–795.
- [64] Shi W, Ji X, Zhang S, et al. Fluorescence chemosensory ultrathin films for Cd^{2+} based on the assembly of benzothiazole and layered double hydroxide. *J. Phys. Chem. C.* 2011; **115**: 20433–20441.