Recent progress in thin film fluorescent probe for organic amine vapour

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There are great needs for real-time detection of volatile organic amines (VOA) through low-cost detection methods in public health, food safety, and environmental monitoring area. Organic thin-film fluorescent probe (OTFFP) is expected to become a new and efficient means of detecting VOA because of its fast response, high sensitivity, no contamination to the analyte and ease to prepare a portable instrument. Compared with the mature detection methods in solution, research on solid fluorescence sensing has been less studied. In this article, we review recent progress in OTFFP research for VOA vapour. We mainly focus on the new fluorescent sensing mechanisms applied in solid state in recent years and the design principle of probes for different types of organic amines (such as primary amine, secondary amine, tertiary amine and aromatic amine). We also review the material structures of these probes and the strategies to enhance their sensitivity or selectivity.

fluorescence, volatile amine, thin-film, probe

1   Introduction

There are urgent needs for sensitive and selective detection of volatile organic compounds with low concentration due to the increasing demand from public health, food safety, environmental monitoring and other related social fields [1]. Particularly, the detection of volatile organic amines (VOA), which were widely used in the agrochemical, pharmaceutical, automotive chemical, cosmetics and food industries, has attracted more and more attention in recent years [2–6]. This is because: (1) some amines are related to certain diseases in metabolic, gastrointestinal, pneumonic and urinogenital system [7,8]; (2) some amines are the main component of drugs such as methamphetamine [9,10]; (3) other amines may be the environmental pollutants in the air.

Therefore, the real-time and on-spot monitoring of these amines is particularly important to control of air pollution and prevention of diseases.

In the past, many successful methods have been developed for the detection of amines in solution, including chromatography [11,12], electrochemical devices [13], colorimetrys [14,15], as well as fluorescence technique [16–18]. However, there still remain challenges for the detection of VOA. The challenges come from many aspects such as the efficiency of vapour capture, affinity of host-guest interaction, and complex components of gas. However, compared with the solution detection, the most obvious advantages of solid state sensing lie in no pollution to the analyte, no additional solvent and simplicity of sampling. Therefore, the study on gas analyte analysis technique is very significant and positive. Luckily, in recent years, there have been a few successful reports about gas amine detection using electronic method [19–21], electrochemiluminescence

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[22], quartz crystal microbalance [23,24], colorimetric [25–28], organic field-effect transistors [29], colormetric array detector [30], ^{19}F NMR [31], and monomolecularly imprinted dendrimer [32,33]. Nevertheless, most of these methods suffer from more or less drawbacks such as complicated operating procedures, low sensitivity, slow response, poor selectivity or expensive detecting device. As a contrast, fluorescent technique is a good method for vapour phase detection because of its simplicity, high selectivity and sensitivity.

Since Professor Swager [34] reported the first example using the *molecule wire effect* of conjugated fluorescent polymer to detect explosive vapour in 1998, organic fluorescent materials have attracted much attention in solid state sensing. So far, the research on p-type material suitable for detection of explosives is far more than the research on n-type material suitable for detection of VOA. This is mainly because organic materials suitable for sensing explosives are mainly electron-donating substances based on photoinduced electron transfer (PET) mechanism. Nevertheless, an electron-accepting conjugated polymer for VOA detection usually has low fluorescence quantum efficiency. This is contradicted with the general rule of sensory materials which should possess considerable emission intensity in the solid state. In addition, unlike the nitro explosives, organic amines can be divided into many categories (including primary amines, secondary amines, tertiary amines and aromatic amine). These amines have subtle differences in properties which makes them difficult to be distinguished. Furthermore, the material for amine vapour detection must meet other conditions, including quick response, good selectivity, and high sensitivity. These factors all restrict the development of the amine vapour sensing material. Fortunately, there are several excellent receptors suitable for solid state sensing by the elaborate molecular design of researchers in recent years. In this review, we will mainly focus on the design strategy and sensing mechanisms of these new probes.

2   Signal mechanisms

As mentioned above, the analyses present different diffusion modes in the solution/film. Thus many conventional fluorescent sensing mechanisms used in the solution cannot be used to illustrate sensing behaviors in the solid state. Here, we summarize the new emerging signaling mechanisms applied in film probe design.

2.1   Photoinduced electron transfer

Photoinduced electron transfer (PET) is commonly used for the electron-donating amines detection. When the electron of the probe on its HOMO is excited to the LUMO, the amine will donate its electron to the HOMO of the probe and hence result in quenched fluorescence, which requires the HOMO level of the amine to be higher than that of the fluorescent probe. The researchers try to design the probes for amines sensing based on PET mechanism by tuning the HOMO energy level carefully.

In 2008, Zang *et al.* [35] firstly reported a strongly fluorescent film probe of perylene bisimide derivatives for detecting vapour amine. This n-type organic semiconductor material **1** (Figure 1) can be fabricated into well-defined nanofibers. Its structure keeps a perfect balance between the molecular stacking and the fluorescence solid state quantum yield. On one hand, its mesh-like film is favorable for enhanced adsorption of the amine molecules. On the other hand, its porous film enables expedient diffusion of guest molecules across the film matrix, leading to high sensitivity and quick response time. The detection limit of the nanofibril film can be projected as low as ~200 ppt for aniline vapour.

In 2009, Liu *et al.* [36] developed a supramolecular assembly fabricated from perylene bisimides and cyclodextrin conjugates. In this molecule, perylene bisimide acts as a fluorescence unit due to its strong solid state fluorescence, photochemical stability and low quantum yield of intersystem crossing. Prmethyl-β-cyclodextrin acts as the molecular receptor that provides the building site for the analyte. The fluorescence of **2** (Figure 1) was quenched 30% by aniline with a vapour pressure of 33 ppm and 15% by toluene with a vapour pressure of 4100 ppm indicating its good selectivity to aniline vapour.

In 2010, Liu *et al.* [37] further reported an asymmetric, amphiphilic perylene bisimide derivative by grafting permethyl-β-cyclodextrin at one side and an octadecyl chain at the other side. To get a sensing film, the aggregates of **3** were embedded in the poly(vinylidenefluoride) (PVDF) membrane from pure methanol and 9:1 water/methanol, respectively. The PVDF-embedded **3** (Figure 1) films from pure methanol and from 9:1 water/methanol show different excimer emissions at 609 and 625 nm, respectively. Because of the distinguishable aggregation states, the vapour sensing performances for different volatile organic compounds are different. In most cases, the fluorescence quenching of **3** from 9:1 water/methanol is more efficient than **3** from methanol.

Based on the above foundations, Liu *et al.* [38] developed another perylene-cyclodextrin conjugate **4** (Figure 1) in 2011. Compared with **3**, probe **4** presented a pronounced improvement of both selectivity and reversibility. The detection limit of **4** for aniline can be predicted to be as low as 80 ppb.

In 2012, Fang *et al.* [39] also developed a stable, ultrasensitive and fully reversible fluorescent sensing film for organic amines by assembling cholesterol (Chol)-derived perylene bisimide **5** (Figure 1) on a glass plate surface. Their study further revealed that both the molecular structure of the probe and the surface morphology of the film are key factors to endow the film with superior sensing perfor-
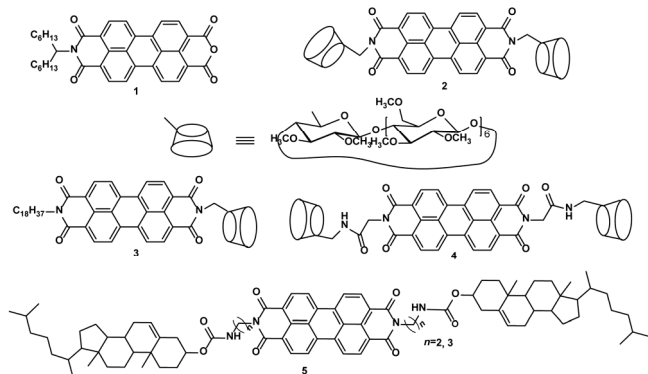
Figure 1 Structures of typical fluorescent film probes **1–6** of perylene bisimide derivatives.

mance for organic amines. The detection limit of probe **5** for amines vapour can be estimated as low as 150 ppt.

2.2 Chemical reaction

Chemical reaction between the object analyte and the sensing material is always an important detection mechanism in fluorescence sensing which leads to significant fluorescence changes via conformational change. The best merits of reactive probes are specificity and cumulative signaling effects. Furthermore, the reactive probe makes it possible to detect analytes at multi-wavelength owing to the emission spectra shift.

As an active functional group, amines may react with many receptors in the solution. Some reactions between the different amines and the receptors are summarized in Figure 2. To get good sensitivity for solid sensing, an eligible reaction suitable for solid sensing should contain several factors: (1) the occurring of the reaction must be quick and without additional activator in the solid-gas interface; (2) the reaction should be finished in a very short time; (3) the structures of new products and the original material should have distinct differences in order to obtain obvious fluorescence signal.
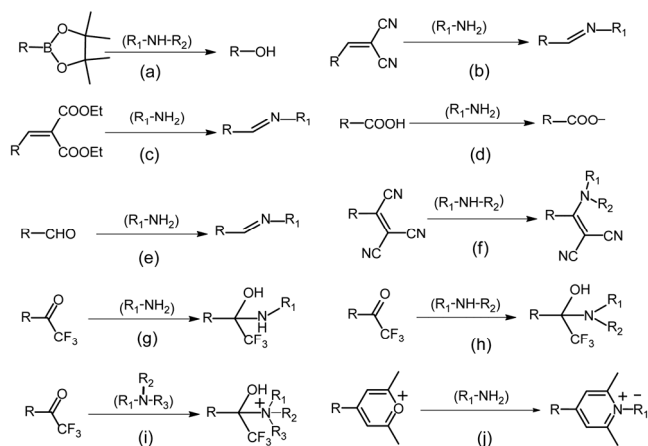

Figure 2 Possible reactions between different amines with receptors.

Besides, the selectivity of the reactive probe is dependent on both the chemical reactivity (i.e. the amine's nucleophilicity plus the steric hindrance of alkyl chains or aromatic rings) of the amine and the amine's lipophilicity that affects its extraction into the lipophilic organic layer.

2.2.1 Irreversible chemical reaction

Our group recently reported an unusual reaction between benzylidenemalonate (BZMA)/benzylidenemalononitrile (BZMN) derivative and primary amine [40]. These two compounds could be converted to benzylidence-propylamine upon exposure to *n*-propylamine vapour without any catalyst in solid state during very short time (<5 min). Using this special reaction, fluorescent conjugated polymer **6** and **7** (Figure 3) were designed and synthesized for primary amine vapour sensing. Polymers **6** and **7** are easy to form porous films on a quartz substrate by drop-casting method. The self-assembly porous structures are advantageous for vapour-phase sensing due to their beneficial surface morphology. After exposure in *n*-propylamine, both the fluorescence spectra and color of **6** and **7** blue shifted. The Stokes shifts of **6** and **7** are 151 and 197 nm, respectively. Such larger Stokes shift could greatly improve the sensitivity to trace quantities of analytes for the larger signal-to-noise ratio and low self-absorption. Further study indicates that **7** has higher sensitivity than **6**.

By combining multi-responsive sites into one molecule, our group [41] recently discovered a new single molecule fluorescent probe **8** which could respond to vapours of multiplicate amines based on specific chemical reactions between the amines and aldehyde/dioxaborolane. The single probe **8** can identify multifarious amines with rapid response and unique triple (absorption spectra, fluorescence color and spectra) output modes. Upon exposure to amines vapours including *n*-propylamine, *n*-hexylamine, benzylamine, aniline, diethylamine and diisopropylamine, both the UV-Vis spectra and fluorescent spectra of **8** films changed a lot. Interestingly, the huge changes in emission spectra were also reflected on the emission color. As shown in Figure 4(a), the films made of **8** present completely distinct colors in the presence of different amine vapours including pink, green, yellow, and orange.
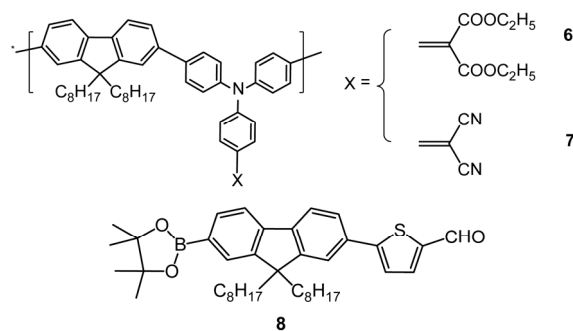
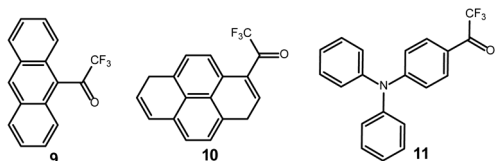**Figure 3** The structures of probes **6–8**.
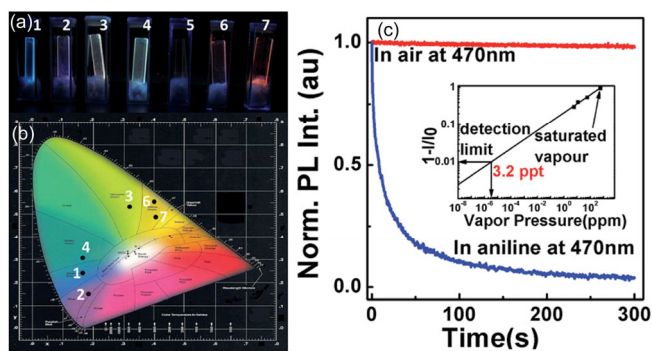
Figure 4 (a) **8** films excited by UV lamp 365 nm after 300 s exposure in air and several saturated organic amine vapour (1 air, 2 *n*-propylamine, 3 *n*-hexylamine, 4 benzylamine, 5 aniline, 6 diethylamine, 7 diisopropylamine); (b) CIE 1931 (*x, y*) chromaticity diagram of the films in the above saturated vapours of different amines; (c) changes in fluorescence intensity of **8** films exposed to air and the saturated aniline vapour for 300 s at 20 °C at their wavelength of the maximum emission. The inset is fluorescence quenching efficiency ($1-I/I_0$) as a function of the vapour pressure of aniline: data (error ±5%) fitted with the Langmuir equation. (a–c) reproduced with permission [41]. Reproduced with permission [41]. (color online)

Besides the different emission colors by naked eyes, the emission colors can also be characterized by their special CIE 1931 color coordinates. With the excellent color-matching between the fluorescence and the CIE chromaticity diagram, amines with similar structures could be further distinguished (Figure 4(b)). The detection limits of this probe to different amines are far below their immediately dangerous to life or health (IDLH) concentrations. For example, the detection limit for aniline can be projected as low as 3.2 ppt which is much lower than its IDLH concentration of 200 ppm (Figure 4(c)).

2.2.2 Reversible chemical reaction

Compared with the irreversible chemical reaction, the reversible chemical reaction brings reversible fluorescence signal change which is more useful for real-time test considering its lower cost.

Very recently, our group reported a series of fluorescent probes with trifluoroacetyl group as the reactive unit and aromatic moieties including anthracene, pyrene and triphenylamine unit as fluorophore for highly reversible, sensitive and efficient amine detection [42]. The chemical reactions that may occur between **9–11** (Figure 5) and amines are described in Figure 2(g–i). On one hand, the trifluoroacetyl group gives the repeatable signal for its fast reversible reactivity with amines. On the other hand, by selecting

suitable aromatic substituent, the reactivity and fluorescent properties could be tuned to afford an efficient amine probe.

Probe **9** emits weak fluorescence both in solution and in film state which is not suitable for sensing. **10** shows strong luminescence and could be rapid and sensitive to detect aliphatic primary and secondary amine vapour except aniline vapour. While **11** is proved to be a simple but effective probe for detecting aliphatic primary amines, aliphatic secondary amines and aniline. The detection limit could be as low as 0.17 ppb for diethylamine and 0.23 ppb for aniline. The probes are characteristic of simple, rapid response, reversibility and high sensitivity which is capable for real-time monitoring of organic amines. As shown in Figure 6, the **11** film has ~95% quenching of its initial fluorescence intensity upon exposure to *n*-propylamine vapour and its fluorescence could be recovered within 15 s just by being exposed to neat air without any heating process or much waiting.

2.3 Organometallic complexes

Crystal inclusion of volatile organic compounds into d^8 and d^{10} metal complexes may affect the fluorescence property greatly through their intermetallic or other weak interactions. Pike *et al.* [43] discovered that copper (I) cyanide networks can bind different amines and the new CuCN-amine adducts would present various luminescence wavelength with the different incoming ligands. Inspired by this discovery, they reported particular and remarkable ligand dependent luminescence behavior upon the fully-reversible reaction of various amines with CuCN. As shown in Figure 7, the emission of CuCN shifted from the dark blue fluorescence into the visible region after surface bonding with different amines and other nucleophilic VOCs. These emission color changes make it easy to differentiate the amines only by naked eyes, offering a simple way for independent monitoring of multiple analytes.

In 2007, Lanza *et al.* [44] found that non-luminescent platinum (II) dithiooxamide species **13** (Figure 8) can adsorb gaseous HCl offering a special ion pair species **12** with strong solid fluorescence. This process is easily achieved by putting **13** into the HCl vapour for a few seconds. The color of solid **13** changes from orange-red to purple-blue immedi-

Figure 5 The structures of probes **9–11**.
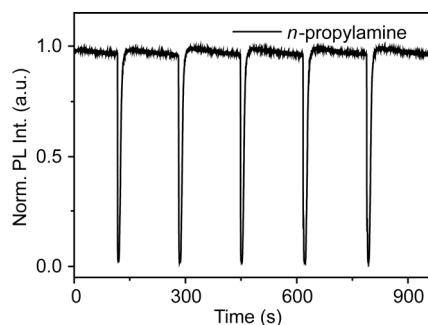
Figure 6 Repeatability of **11** film exposed to *n*-propylamine vapour, the emission intensity was monitored at 525 nm. Reproduced with permission [42].
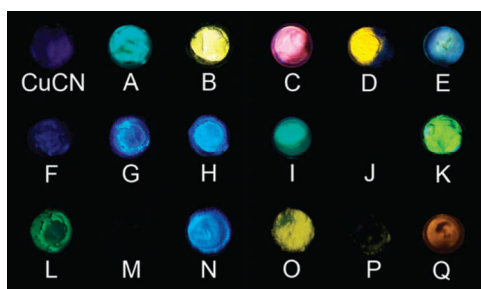
Figure 7   Luminescence of CuCN+liquid L under 254 nm light at room temperature. A: piperidine; B: *N*-methyl piperidine; C: *N*-ethyl piperidine; D: *N*-methyl pyrrolidine; E: *N,N*-dimethyl cyclohexylamine; F: trimethylamine; G: *N*-methyl morpholine; H: *N*-methyl piperazine; I: *N,N*-dimethyl piperazine; J: pyridine; K: 2-methyl pyridine; L: 3-methyl pyridine; M: 4-methyl pyridine; N: 2-ethyl pyridine; O: 3-ethyl pyridine; P: 4-ethyl pyridine; Q: 4-ᵗbutyl pyridine. Reproduced with permission [43]. (color online)
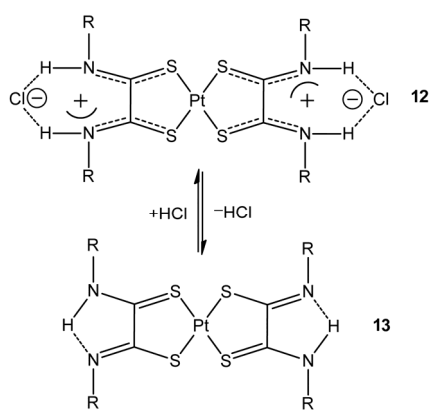
Figure 8   Structural formula of **12** and **13** and their conversion scheme. R is butyl. Reproduced with permission [44].

ately. At the same time, the fluorescence became much stronger. Furthermore, this process could be quantitatively repeated upon exposure to ammonia vapours or by heating. This findings make **12** a potential candidate for ammonia gas sensor.

Leznoff *et al.* [45] reported four polymorphic forms of complex $Zn[Au(CN)_2]_2$. Three of the four polymorphs are luminescent, containing solid-state emissions with wavelengths ranging from 390–480 nm. Upon exposure to ammonia vapour, the structures and emission energies of the polymers changed, with the emission wavelength shifting to 500 nm for $Zn[Au(NH_3)_2(CN)_2]_2$, which adopts a two-dimensional layer structure with octahedral, trans-oriented NH_3 groups. The detection limit of NH_3 vapour is as low as 1 ppb. Desorption of ammonia occurred over 30 min at room temperature.

2.4   Cationic conjugated polymer combined with negative ion or polymer

Conjugated polymer has attracted much attention in fluorescent solid sensor because the efficient exciton migration

in these materials may bring sensitivity enhancements. In the past, many efforts have focused on electron-donating polymer to detect electron-accepting analytes such as nitro explosives. In contrast, the electron-accepting polymer has been reported by a few examples although smart design has been concerned including carefully adjusting the energy level and significant synthetic effort.

Swager's group [46] recently reported a series of conjugated cationic polymers combined with their accompanying counter-anions. These complexes can selectively differentiate a series of industrially relevant amine gas. The optical properties of polymer **14–17** (structures shown in Figure 9) are similar indicating a little influence of the counter-anion. The sensory polymer such as **17** shows good response to aniline vapour with a linear relation to the concentration of aniline. And the polymer film is regenerative just by exposure to the air-flow for 10–15 min. The researchers also selected a series of industrially relevant amines to test the specificity of these polymers to amines. The resulting data indicate: **16** is the most sensitive probe to simple alkyl amines; **14** is more responsive to pyridine and **17** is more suitable for aniline detection. The detection limits of these polymers can all reach ppm level. Especially, aniline, cyclohexylamine, and triethylamine could be detected at concentrations below their permissible exposure limit which is meaningful in real test.

In 2014, Yashima *et al.* [47] developed a chiral turn-on fluorogenic sensory system for detection of primary amine and secondary amines. The starting film A was prepared using a protonated riboflavin **18** and riboflavin-derived cationic polymer **19** immobilized in a poly(vinyl chloride) film. The self-standing fluorescent film A was converted to the nonfluorescent film B by treating with aqueous $HClO_4$ in diethyl ether. As shown in Figure 10, when film B was exposed to 2-propylamine vapour for 5 s, the film C was formed rapidly together with the greenish yellow fluorescence of 35-fold enhancement. Exposure to other secondary and primary amine vapours, the similar fluorescent changes along with the color changes were observed. Other volatile vapours including tertiary amine, ether, ester, amide, alcohol and thiol brought no fluorogenic and colorimetric responses. Film C could be reversibly converted to the original non-fluorescent film B through elimination of amines by treatment with aqueous $HClO_4$ in diethyl ether, then the renewed film B could further sense amines again. The cycle could be repeatable at least three times. The most
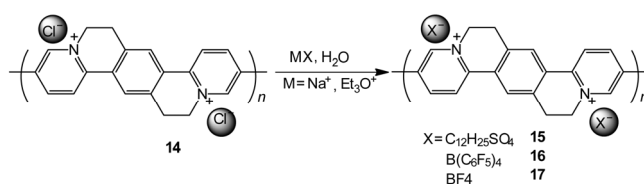
Figure 9   The structures of **14** and anion metathesis reactions producing adducts **15**, **16**, and **17**. Reproduced with permission [46].
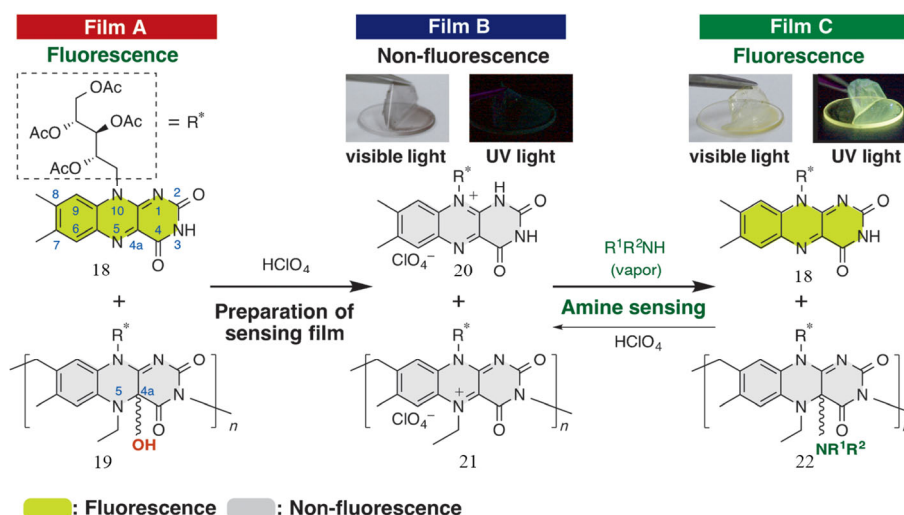
Figure 10 Conversion of fluorescent Film A to nonfluorescent Film B and reversible interconversion between Film B and fluorescent Film C. Film A consists of fluorescent **18** and nonfluorescent **19** immobilized in a PVC film by treatment with aqueous $HClO_4$. The nonfluorescent Film B becomes fluorescent Film C upon exposure to primary and secondary amine vapours due to the formations of fluorescent **18** again, which is further converted to the nonfluorescent Film B by treatment with aqueous $HClO_4$. Photographs of Film B and Film C (R^1R^2NH=2-propylamine) under visible (left) and UV light (λ_{ex}= 365 nm, right) are also shown. Reproduced with permission [47]. (color online)

attracting point of this system is that it is the first time to detect the chirality of the enantiomeric amine vapours visually.

2.5   Binding-induced weakening of internal heavy-atom effect

For many organic fluorescent materials which contain heteroatom, internal heavy-atom effect is ineluctable. The existence of heavy-atom usually quenches the fluorescence of organic materials. Because heavy-atom such as sulfur atom can strengthen spin-orbit coupling and bring efficient inter-system crossing leading to a low fluorescence quantum yield. This phenomenon is not favorable for the probe based on "turn-off" mechanism.

However, think of it from another perspective, it may present a promising molecule design strategy of "turn-on" mode if the heavy-atom effect is deliberately weakened. "Turn-on" type detecting mechanism has many advantages than "turn-off" mechanism such as not easily affected by oxide substances and not affected by "concentration quenching".

Fu *et al*. [48] thus reported a single fluorene-thiophene-based compound/polymer (**23** and **24**) to detect methamphetamine through fluorescence enhancement in 2013. Both **23** and **24** emit poor fluorescence in film due to the existence of sulfur atom in the thiophene unit. However, when amines such as methamphetamine binds with receptors **23** or **24**, their interaction will weaken the internal heavy atom effect and cause fluorescent enhancement. It is noteworthy that the probe **23** and **24** both show high selectivity to methamphetamine compared with other common amines. The good selectivity was attributed to the unique structure

of methamphetamine. In methamphetamine molecule, there exist both imine group and phenyl group. On one hand, as a good electron donor, the imine can reduce the heavy atom effect after binding with thiophene. On the other hand, the phenyl can form the enhanced intermolecular ordering and π-π^* stacking with the sensor molecule. Taking a fluorescence intensity change as 1%, the detection limits of **23** and **24** (Figure 11) for methamphetamine vapour were estimated to be 1.9 and 6.4 ppm.

2.6   Two-component organogel

In 2013, Lu's group [49] presented a hydrogen complex which could self-assemble into one-dimensional fibers in its gel phase. This gelator is composed of one 1,4-bis(2-(pyridin-4-yl)vinyl)-benzene (**25**) and two *N*-lauroyl phenylalanines (**26**) and is linked by two OH···N hydrogen bonds between the carboxylic acid groups and the pyridine units (Figure 12).
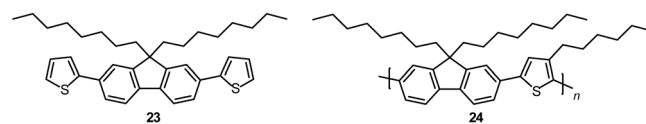
**Figure 11**   The structure of probes **23** and **24**.
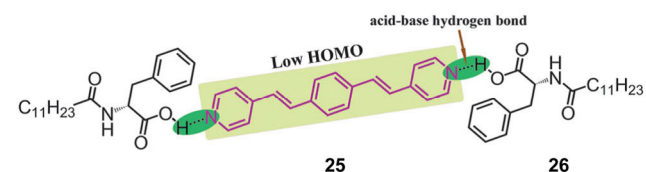
Figure 12   The structures of **25** and **26**. Reproduced with permission [49].

A sensing film of approximately 740 nm thickness was obtained by casting **25** and **26** in their cyclohexane solution on a glass slide, followed by a slow evapouration of the solvent. As shown in Figure 13(a), upon exposure to aniline vapour (329 ppm), the fluorescence of the xerogel film was quenched by almost 98% within as short as 0.8 s regardless of large sensing film thickness. The fast response time is mainly due to the 3D continuous, porous structure of the xerogel film, which allows expedient diffusion of the aniline molecules. The detection limit of the sensing film for aniline can be as low as 1.8 ppb. And such a process is reversible.

Different with exposure in aniline vapour, upon exposure to *n*-butylamine, the fluorescence of the prepared film changed from yellow-green to blue, with the emission peak at 544 nm disappeared and a new blue emission band peaked at 440 and 460 nm emerged (Figure 13(b)). However, this sensing process is irreversible.

Both the UV-Vis absorption and IR spectra suggest that aniline was absorbed physically on the surface of nanofibers and *n*-butylamine destroyed the hydrogen-bonded complex and released **25** by deprotonating carboxylic acid. Thus the fibrous film could be used as a sensor to discriminate aromatic and aliphatic amines.
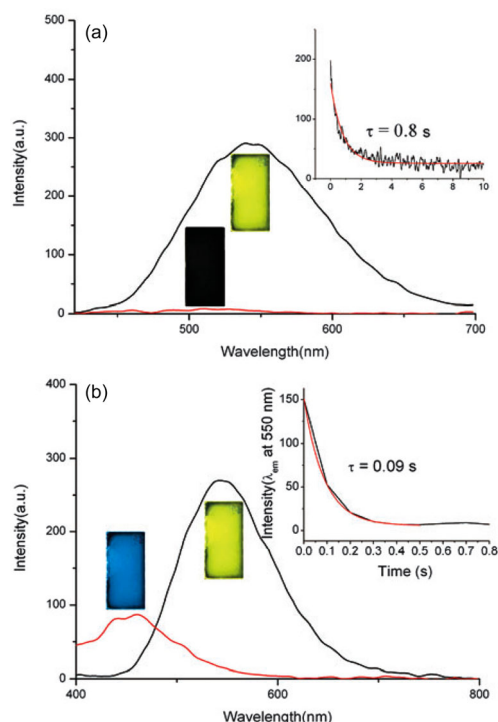
Figure 13 Fluorescence spectra of the cyclohexane xerogel film deposited on a glass slide before (black line) and after (red line) exposure to aniline vapour (329 ppm) (a) and *n*-butylamine (80000 ppm) (b) for 30 s. The insets show the time-course of fluorescence quenching of the xerogel film after being added into a cell filled with the vapours of aniline and *n*-butylamine; the intensity was monitored at 550 nm. Reproduced with permission [49]. (color online)

2.7 Changes on aggregation induced emission (AIE) phenomenon brought by solvent

In 2011, Coughlin *et al.* [50] synthesized a kind of polyfluorene material containing *o*-carboran **27** (Figure 14). This polymer was found to display AIE behavior, showing green photoluminescence in the solid state resulting from the AIE of the fluorene segments adjacent to the carborane cages. The emissions can be modulated through interactions with solvent molecules which provides a new way toward conjugated polymer sensors. In the film state, theo-carborane poly- (fluorene) was found to undergo an emission wavelength shift upon exposure to different organic solvent vapours, along with the fluorescence color changing from bright green to shades of blue, yellow or orange in the presence of triethylamine, diisopropylamine, *n*-butylamine, pyridine, 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU), aniline, and piperidine. The obvious shifts were related to the polarity of the solvent. The solvents with more polar produced larger red-shifts, similar to solvochromatic shifts observed for fluorescent molecules in the solution phase. The presence of amines influenced the AIE and added possibility of further quenching the emissions. The sensing behavior is reversible upon removal from the vapours.

3 Differentiation of different types of amines

Organic volatile amines are comprised by many kinds of amines, including primary amines, secondary amines, tertiary amines, and aromatic amine. These organic amines have their individual use in pharmacology or environmental science. Thus differentiation of these amines has important significance. However, there are still many challenges to selectively detect these amines because of the scarcity of smart materials capable of binding analytes through strong interactions in the solid state. Herein, we give several typical examples for detection of these amines.

3.1 Primary amine

As mentioned above, our group once discovered an unusual
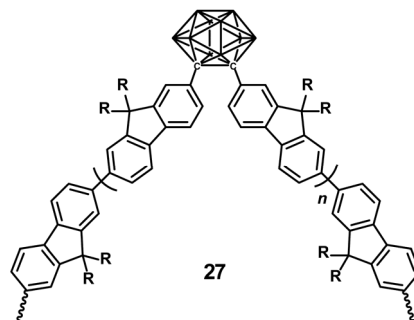
Figure 14 The structure of probe **27**.

irreversible chemical reaction between benzylidenemalonate (BZMA)/benzylidenemalononitrile (BZMN) derivative and primary amine [40]. Using this reaction, we have successfully realized the selective detection of primary amine.

In 2013, Tang *et al.* [51] found that the fluorescence of a pyrrole derivative, 4-(2,5-diphenyl-1-pyrrolyl) benzoic acid could be repeatedly transformed between "off" and "on" states by absorbing with primary amines vapour and heating processes. This phenomenon makes such a material to be a promising fluorescent probe for rapid, sensitive and selective detection of gaseous primary amines.

Compound **28** (Figure 15) emits weak fluorescence both in solution and in solid. The reason for its poor fluorescence (FL) quantum yield in the solution is mainly due to the active rotation of its peripheral phenyl rings which leads to the energy effectively consumed through nonradiative relaxation channel. In the aggregated state, a dimer will be formed when one molecule is excited. Its nonradiative relaxation quenches the light emission of the luminophore. Since the dimer formation is responsible for the solid fluorescence quenching, there must be some way to make the fluorescence recovered if the dimer structure is broken by external stimuli.

As an organic alkali, amine can bond with carboxylic acid group through the hydrogen bond. Thus the presence of organic amines vapour can improve the fluorescence of the **28**. As forecasted, the $\varPhi_{FL}$ value of **28** solid powder was enhanced from 4% to 52.4% after being exposed to butylamine gas. However, the secondary amine and the tertiary amine vapours have no effect on the FL process. The plot of emission intensity versus amine concentration gives a straight line with a detection limit of 3 mmol/L and a correlation coefficient of 0.9877.

3.2 Secondary amine

Till now, the special probes for secondary amine have been rarely reported. This is mainly due to the structural difference between aliphatic primary amine and secondary amine resulting in their different chemical reactivity. Fu *et al.* [52] accidently discovered that secondary amine could accelerate the photo-oxidation of arylboronates (or aryl boronic acids) to corresponding phenols. Therefore, boronate ester unit can be chosen as the reactive recognition part in the fluorescent sensing of secondary amines.

There are three pivotal units in compound **29** (Figure 16): boronate ester, fluorene and 4,4-difluoro-4-bora-3a,4a-
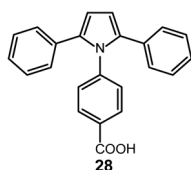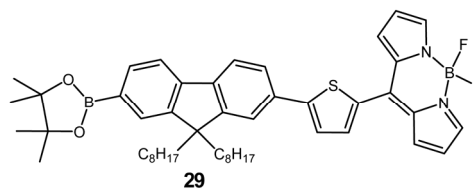
Figure 16   The structure of probe **29**.

diaza-*s*-indacene (BODIPY) derivatives which act as identification part, fluorescent group and chromophore, respectively. This BODIPY-based probe exhibits both color and fluorescence response to secondary amines either in solution or in film even in the form of test papers exhibiting its wide potential applications. Besides, the probe showed remarkably high selectivity to secondary amines over other amine species. The detection limits of this probe for diethylamine and diisopropylamine vapours can be estimated to be 1.85 ppb and 2.42 ppm, respectively.

3.3 Tertiary amine

Till now, the selective fluorescent probe just for tertiary amine vapour has been scarcely reported. In 2010, Takagai *et al.* [53] reported cross-linked acrylic ester microparticles (EG50OH) with absorbed fluorescent probe molecules, such as fluorescein and acridine orange employed as "turn-on" fluorescent sensors for the detection and determination of ammonia and organic amine vapour concentrations. The response is based on the acid-base properties of the fluorescent probe molecules. The fluorescent probes immobilized in/on the EG50OH only exhibit weak fluorescence. Upon exposure to ammonia or amine vapour, the fluorescent species are deprotonated and exhibit much stronger fluorescence owing to exposure to these basic analytes.

The probe responded to organic amines following the order: trimethylamine>*tert*-butylamine>diethylamine>*n*-propylamine>ammonia which indicated certain selectivity to tertiary. A limit of detection of 0.048 ppm for triethylamine vapour was achieved using this probe. And the detection limit achieved for ammonia vapour was 0.73 ppm, the response being linearly dependent on concentration over the range of 1.0–250 ppm gaseous ammonia.

3.4 Cycloaliphatic amine

In 2000, Yoshida *et al.* [54] discovered that benzofuranoquinol clathrate host exhibited both color and fluorescence changes upon exposure to various gaseous amines either in the crystalline state or in the film state. Using this phenomenon, they prepared the benzofuranoquinol thin film on glass plates by a conventional vacuum-vapour deposition method for monitoring amine vapour. Upon exposure to amine vapours, the long-wavelength absorption of sensing material decreased and a dramatic fluorescence enhance-

Figure 15   The structure of probe **28**.

ment with a blue-shifted emission maximum were observed. The response time for the optical sensing was fast in the thin-film state with a saturation time within 10–20 s. The degrees of the fluorescence enhancement and the blue-shift of emission wavelength are dependent on the enclathrated amine molecules and increased in the following order: *N*-methylpiperazine>piperidine>*N*-methylmorpholine>morpholine>diethylamine>ethylamine, suggesting the selectivity to cycloaliphatic amine. The formation of clathrates (host: guest=1:1) was testified for all the above amines from NMR integrations of the dissolved samples prepared from the exposed thin-films. The host-guest complex formation is particularly interesting from the viewpoint of developing novel chemosensors or new emissive materials **30** (Figure 17).

They further investigated the solid-state photophysical properties of the guest-free and amine-inclusion clathrate compounds in another report [55]. Similar fluorescence enhancement, blue-shift of the absorption and fluorescence wavelength maxima were observed. The X-ray crystal structures of the guest-free and clathrate compounds indicated that the intercalary molecules break the intermolecular hydrogen bonds and enlarge the distance between the host-host aromatic planes. It is also confirmed from the spectral data and the X-ray crystal structures that the destruction of the host-host π-π interactions by the inserted amine molecules is the main reason for the guest-dependent fluorescence enhancement behavior. These results are beneficial for the design of new solid probe.

3.5   Aromatic amine

Aromatic amines such as aniline are toxic organic compounds whose main uses are the precursors of polyurethane and other industrial chemicals. Its chemical property is completely different with aliphatic amine. Compared to aliphatic amine, aromatic amine could be more easily detected through PET mechanism.

In 2009, Zang *et al.* [56] studied the fluorescence sensing of the film fabricated from *N*-(1-hexylheptyl) perylene-3,4,9,10-tetracarboxyl-3,4-anhydride-9,10-imide by a new self-assembly approach, although this material had been reported earlier. In this report, they emphasized on the relationship between the size of the nanofibers and the sensing property. They discovered that the nanofibers with the diameter of 30–50 nm possessed much better sensitivity than that of 350 nm. This is because the smaller size of nanofibers is helpful for enhancing the porosity of the film. They are prone to producing a smaller pore structure but

with a more bulky inter-pore connection. Such enhanced porosity, together with the enlarged surface area, not only accelerates the adsorption of amine vapour, but also strengthens the accumulation of the amine species collected from the gaseous phase. The detection level for the 0.35 mg film is predicted at ca. 1 ppb if the fluorescence intensity changes by 1%. Whereas for the 0.15 mg film, the value can be as low as 0.1 ppb. In contrast, for the film deposited from 0.35 mg large fibers (350 nm diameter) the detection level is up to 5 ppb.

3.6   Special amine

Here, the special amine means that the amine including aromatic ring, aliphatic chain and amine unit is connected with aromatic ring indirectly. Among these amines, methamphetamine (MA) is a famous man-made drug which brings significant impacts on human health and social security. Existing detection technologies such as GC-MS, liquid chromatography, immunological methods, thin-layer chromatography (TLC), electrochemiluminescence and immunoassay screening method cannot meet the needs of the rapid detection on the spot.

In 2012, our group [57] demonstrated three fluorene-based conjugated polymers **31–33** (Figure 18) for MA detection. Electron-withdrawing groups 2,1,3-benzothiadiazole-4,7-diyl (BTD), 2,1,3-benzooxadiazole-4,7-diyl (BOD), and 1,4-benxodiazine-5,8-diyl (BDZ) were selected as the acceptor in order to finely tune the HOMO level of the polymer. The fine structural tuning could not only adjust the PET between the polymer and MA but also affect the bonding force to MA. Their fluorescence quenching responses to different amines were demonstrated arising from the photo-induced electron transfer. Meanwhile, the fine tuning of the bonding force resulted in different sensitivity and selectivity of the polymers. Among them, polymer **31** with benzothiadiazole showed the best selectivity and sensitivity to MA vapour with a detection limit of 180 ppb. And ~20% fluorescence could be quenched/recovered within 2 s upon exposure to MA and air in sequence.

Although fluorescent conjugated polymer (CP) sensor possesses the merits of extremely high sensitivity and easy signal transduction, designing a highly efficient CP often exhausts many efforts by tuning the HOMO level. He *et al.* [58] thus presented a "turn on" mechanism in the vapour-phase detection of vapour phase electron donating amines via tetraphenylporphyrin or metallophenylporphrin doped polyfluorene.
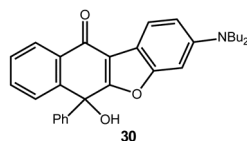
As shown in the proposed sensing scheme (Figure 19(a)),

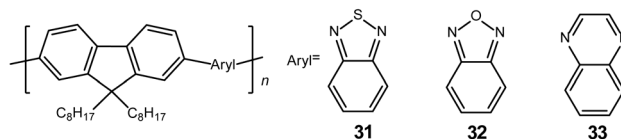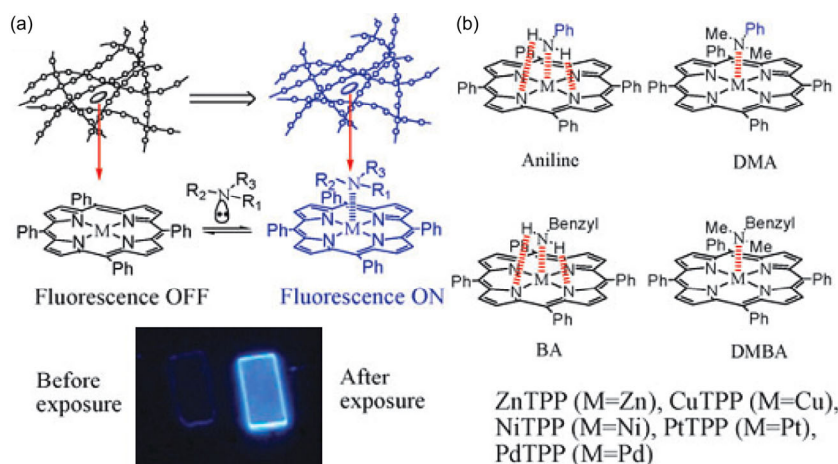**Figure 17**   The structure of probe **30**.

Figure 18   The structures of probes **31–33**.

Figure 19 (a) Schematic representation of "turn on" mechanism in the vapour-phase detection of electron donating amines; (b) molecular structures and different bonding interactions of aniline, *N,N*-dimethylaniline (DMA), benzylamine (BA), and *N,N*-dimethylbenzylamine (DMBA) with MTPP. Reproduced with permission [58].

the fluorescence of poly(9,9-dioctylfluorene) (PFO) was efficiently quenched by tetraphenylporphyrin (TPP) or metallotetraphenylporphyrin (MTPP) via electron/energy-transfer in the solid state firstly, upon contacting with amine, the reversed electron/energy-transfer between the amines and the TPP brought on fluorescence recovery once electron donating amines bound with TPP or MTPP.

In contrast with other MTPP or TPP, PdTPP showed larger quenching efficiency to PFO film. In addition, different amines have different electron donating ability as well as diverse binding intensity with MTPP. So the PFO doped PdTPP showed discrepant selectivity to different amine. Upon exposure to MA, the fluorescence of PdTPP/ PFO film increased quickly with the fluorescence enhancement of over 10-fold. Other solvents such as aniline, ammonia, hydrazine CH_2Cl_2, acetone, ethanol, acetonitrile and nitrobenzene had no responses. This phenomenon indicates that PdTPP doped with PFO is a potential material for MA sensing.

4   Typical strategies to enhance sensitivity or selectivity

A successful chemsensor should possess both high sensitivity and good selectivity. Different to the detection in the solution, the solid state sensing depends on not only the molecule structure but also the size and morphology of the nanostructures on the substrate. To improve the sensitivity or selectivity, smart strategies should be developed to fabricate organic nanostructures with different morphologies or construct special chemical structure.

4.1   Self-assembly nanofiber

Nanofibers possess merits such as large surface area to

volume ratio, flexibility, and superior mechanical performance. These excellent characteristics make the materials which can form self-assembly nanofibers good candidate for fluorescent probe, because the materials with high surface-to-volume ratios usually have extra sensitivity to the analytes adsorbed on the surfaces. Also the large interspace in the ultrathin nanofibrils would favor the enhanced adsorption, accumulation and diffusion of gaseous molecules. In addition, the amplified fluorescence signal may be gained by the enhanced intermolecular exciton diffusion along the long axis of the 1D nanostructure.

In recent years, some fluorescent probes which can form self-assembly fiber films have been developed to detect organic amine vapours because of their high sensitivity. In 2011, Lu *et al.* [59] reported new triphenylamine functionalized bis(dioxaborine)carbazole derivatives **34–36** (Figure 20). They discovered that the low-dimensional nanostructures indicated different morphologies such as single-crystalline nanowire, amorphous nanoparticles and nanofibers with carbon chains of different lengths (*n*=4, 8, 16).

The mesh-like film obtained from *n*=16 based gel exhibited faster fluorescent response in milliseconds and higher sensitivity than the nanoparticle- and nanowire-based film. Because the obtained super molecular obtained in the gelling process percolates and fills the entire volume at a low-over all-volume fraction, and the entangled piling of the fibers leads to increased porosity. Thereby it not only provides a large surface for enhanced adsorption and accumulation
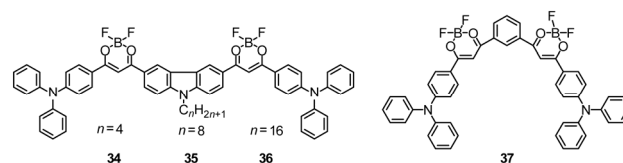
Figure 20 The structures of probes **34–37**.

of gaseous molecules but also enables expedient cross-film diffusion of gaseous species. The probe shows high sensitivity to aniline vapour with a detection limit of 8.6 ppm.

In 2012, Lu's group [60] further found that the boomerang shaped-diketone-boron difluoride **37**, with a lower molecular weight is also preferred to self-assemble into 1D nanofibers in an organogel phase directed by balanced π-π interactions. These nanofibrils show high sensitivity to aniline vapour as low as 100 ppb. The nanofibrils also show obvious fluorescence quenching upon exposure to other VOA (including *n*-butylamine, dibutylamine, tributylamine, triethylamine, cyclohexylamine, hydrazine and *N,N*-dimethylaniline). They deduced that the sensing mechanism was attributed to the interaction between the lone electron pairs of the nitrogen atom in amine and the orbital of boron which could be proved by ^{11}B NMR. The sensing process was approved to be reversible after the sensing film was exposed to air for 10 min.

### 4.2   Ordered assembly arrays of ZnO nanorods to enhance the sensitivity

Not only self-assembly nanofiber of material itself, but also using substrate with special nano structure can improve the sensitivity of film probe.

In 2011, our group [61] reported unique ordered assembly arrays of ZnO nanorods (Figure 21). This assembly nanorod combines merits of single fibers and clusters, possessing identical orientation, large surface-to-volume ratio, evanescent transmission, and evanescent coupling. When the sensing material was coated on the assembly arrays, it generated amplified spontaneous emission (ASE) action. For example, the fluorescence intensity of the narrowed spectrum can be 52.4-fold enhanced. Further sensing experiments indicate that sensors based on the assembly arrays displayed 100% elevated normalized quenching rate and

several times longer full load time compared with reference sensors. This work provides a facile method to fabricate secondary structures of 1D rigid material and presents a new way to design highly sensitive optic sensors. Moreover, evanescent excitation caused ASE action of fluorescent organics, and the correlative sensitivity gain is of interest in both theoretical research and the applications field.

4.3   Branch effect and aggregation control of the sensing performance

Branched molecules are typically symmetric around the core, and often adopt a spherical three-dimensional morphology. This may endow them unique characteristics in chemical sensing. In 2012, He *et al.* [62] reported a series of benzothiadiazole-pyridine branched triphenylamine derivatives **38**, **39**, **40** (Figure 22) to detect aniline vapour. The sensing mechanism is based on photoinduced electron transfer (PET). The fine controlled energy levels ensure the high selectivity to aniline for all three sensory materials. However, with the increasing of the branch numbers, the aggregations of the three materials in the film state on a quartz substrate intensify. The self-aggregation brings about fluorescence quenching, reduces the contact probability and vapour penetration between the material and analyte vapour which are all unfavorable for fluorescence sensing. To decrease the self- aggregation and study the intrinsic property of these materials, the oriented ZnO nanorod array is introduced as the substrate. Interestingly, the sensing performance of materials is enhanced with the increasing of branches numbers through the cooperative effect of branch-effect and special substrate with high surface-to-volume ratio and 3D structure. Fluorescence intensities of the films on the nano-substrate are 34%, 45% and 54% quenched for **38**, **39** and **40**, respectively, after exposure to 300 ppm aniline vapour for less than 5 s. In addition, the fluorescence of all three
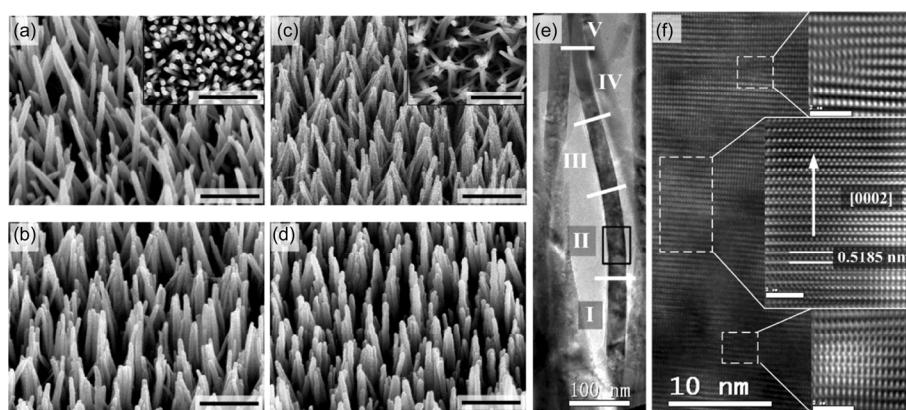
Figure 21   SEM images of ZnO arrays of fastigiate assembles (AFAs) grown for 5 h (a), 6 h (b), 7 h (c), and 8 h (d) with 500 nm scale bars. Inset of (a) is the top view image of ZnO nanorods grown without PVA; inset of (b) is the top-view image of the 6 h grown AFAs. (e) TEM bright field image of a typical ZnO nanorod. (f) High-resolution TEM image of the section marked in (e). Insets are the inverse Fourier transform images of correlating areas as marked, respectively indicating edge dislocation regular lattices and screw dislocation in the ZnO crystal (from top to bottom). Scale bars in the insets are 2 nm. Reproduced with permission [61].
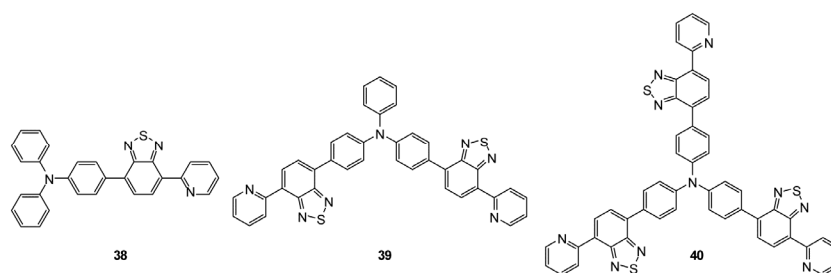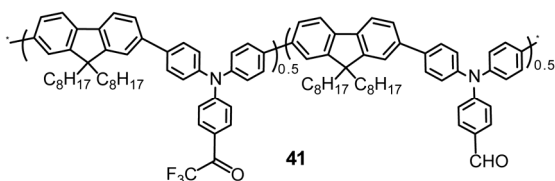
Figure 22 The structure of probes **38–40**.

sensory materials is almost completely recovered by eluting with fresh air for 20 s. The detection limits are predicted to be 1 ppm, 100 ppb and 1 ppb for **38**, **39** and **40**, respectively, demonstrating a significant effect of the molecular branches.

4.4 Strategy to detecting multiple amines using single probe

Design of selective probe for some special amines has certain difficulty. Nevertheless, the detection of a variety of amines simultaneously with a single probe is more difficult. Currently detection of multifarious VOA is mostly based on sensing array detector. Although this method has certain selectivity, it also produces cross-talk, large invasive effect and different location, making the detecting behavior unsuitable for quantification.

Single fluorescent probe capable of responding to various amine gases synchronously is urgently desired. To construct a one-to-many detecting probe, an effective way is to combine multiple specific receptors or reactive moieties into a one molecule or conjugated polymer backbone. Based on this cognition, Fu *et al.* [63] recently proposed a new thin film fluorescent probe for different volatile amines. **41** (Figure 23) was synthesized by incorporating the aldehyde and trifluoroacetyl reactive units into conjugated polymer backbone. Its films can realize the fingerprint fluorescence detection of three types of amines vapours (including aliphatic primary amine, aliphatic secondary amine and aromatic amine) and their mixtures with a change in emission color or fluorescence quenching with excellent reversibility by the cooperative effects of the two reactive functional groups. The detection limits of this probe to different amines are all below their immediately dangerous to life or health (IDLH) concentrations. For example, the detection limit for *o*-toluidine can be as low as about 0.55 ppt, which is much lower than the IDLH concentration of 50 ppm.

Figure 23 The structure of probe **41**.

5 Conclusions and perspectives

In summary, although there emerged a few excellent probes for VOA vapour in recent years, the study on this area still requires a much-needed boost. The main challenges are as follows: (1) Discriminating organic amines with similar structure is difficult. For example, the high selective fluorescent solid probe for tertiary amine vapour has not been reported. (2) Compared to the detection in the solution, the mechanism of gas phase detection for amine is still imperfect.

To meet the requirements of sensitivity and selectivity in solid sensing, smart strategy should be addressed on these elements: (1) Rational-designed molecule structures need to be developed. A simple probe that can respond to many analytes with reversible signals is undoubtedly most popular. (2) Profitable surface morphology should be obtained. Here, the surface morphology control includes both the sensing molecular morphology and the morphology of the substrate. To get a better understanding of these two factors, which have effects on the self-assembling process of conjugated organic molecules, and the prediction of the microstructures in organic nanomaterials, is still a great challenge. (3) Suitable mechanisms are selected to apply in solid state. At present, many weak interactions such as metal-solvent bonds, acid-base interaction, metallophilic contacts, π-π stacking, hydrogen bonding and host-guest interaction together with the isomerization induced by reversible/irreversible chemical reaction can all be used in vapour sensing. Particularly, the vapour-triggered luminescence colour changes are most fascinating.

Overall, any favorable elements for solid sensing are apt to pull in molecular design in the future. The development trend of the solid fluorescence sensor lies in not only using single molecules, single sensing mechanism , but also using composite material, multiple sensing mechanism to give full play of their synergistic effect to improve the sensitivity, stability and selectivity.

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