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ARTICLE TYPE

Highly efficient single fluorescent probe for multiplicate amines vapours via reaction between amine and aldehyde/-dioxaborolane

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A fluorescent probe with multiplicate reactive groups which can detect vapours of different primary amines and secondary amines simultaneously with fast response in seconds and high sensitivity at ppt~ppm levels was realized.

There are exigent needs for sensitive and selective detection of volatile organic amines because of their wide existence in industrial process management, chemical threat detection, medical diagnostics, food quality control and environmental monitoring. [1] Among them, some amines are important marker species for diseases of metabolic, [2] gastrointestinal, [3] pneumonic [4] and urinogenital system. [5] And some others may lead to serious air pollution. [6, 7] Many traditional analytical methods including gas chromatography and mass spectrometry, however, usually involve disadvantages such as complicated operating procedures, slow response and high costs. Therefore, it is of great importance to develop highly selective, sensitive, convenient and rapid detection methods for amines.

Optical sensing of organic amines vapours has received considerable attention due to its high specificity, sensitivity and ease of handling. At present, two main strategies for the design and preparation of intelligent materials for amines vapour detection have been reported. One is focused on controlling and tuning the molecular packing mode to acquire self-assembled fibrous films [8] and the other is utilizing the sensing array detector. [9] Nevertheless, most of the former probes are based on photo- induced electron transfer (PET) mechanism or other weak interaction which usually show poor selectivity [10, 13] or response to individual species.[14] As for sensing array detector, just as pointed out by Suzuki et al., the combination of several fluorescent probes produces cross-talk, large invasive effect, different location, and different metabolisms, making the detecting behavior unsuitable for quantification.[15] Therefore, it is still a big challenge to detect multiple amine vapours simultaneously and a single probe capable of responding to various anylates concurrently is urgently desired. More recently, by combining two responsive sites into one molecule, Lin and coworkers successfully presented a single-fluorescent molecular probe for H_2O_2, NO and H_2O_2/NO with three different sets of fluorescence signals.[16] Such fluorescent probe opens an opportunity for solving the pivotal problem in the simultaneous detection of various amines. Aldehyde group, as a famous unit which can easily form imine with primary amine through Schiff base reaction, can be selected as the recognition part for primary amine. Besides, we recently reported that the secondary amine can accelerate the photooxidation of arylboronate to yield the corresponding phenols. [17] Therefore, the arylboronate could be adopted to act as the recognition unit to identify secondary amines.

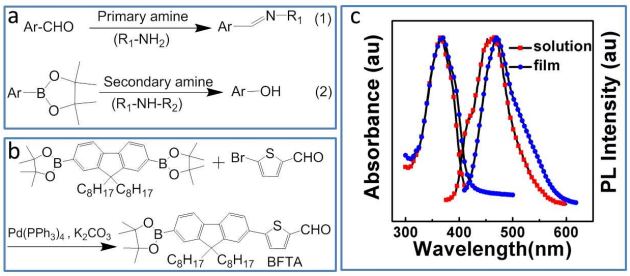

Fig. 1 (a) Reaction mechanism between aldehyde and primary amine as well as arylboronate and secondary amine (b) Preparation of probe BFTA (c) Normalized UV-vis absorbance and fluorescence spectra of BFTA in THF solution(red) and in films (blue).

Herein, we present a new single molecule fluorescent probe BFTA which could respond to vapours of multiplicate amines based on specific chemical reactions between the amines and aldehyde/ dioxaborolane (Fig. 1a). This single probe can identify multifarious amines with rapid response and unique triple (absorption spectra, fluorescence color and spectra) output modes.

BFTA was prepared according to the synthetic route as shown in Fig. 1b. Its structure was well characterized using NMR and MS spectroscopies. The maximum absorption and emission peak are located at 366 nm and 466 nm, respectively, in dilute THF solution (1×10^{-5} M) (Fig. 1c). Compared to those in the solution, the maximum absorption and emission peak in the solid state showed a little red shift to 369 nm and 470 nm, respectively. It suggests the intermolecular π-π interaction between BFTA molecules is not so strong upon assembly into the solid state which is favorable for solid state sensing. The fluorescence quantum yield of BFTA, which was estimated with 9, 10-diphenylanthracene as reference standard, is 11 % and the molar extinction coefficient is 35,800 M^{-1} cm^{-1}.

Since the target analyte is amine vapour, we focused our research on the sensing performance of BFTA in the solid state. We prepared BFTA films by spin-coating its THF solution (1×10^{-3} M, 1×10^{-2} M and 1×10^{-1}M) on the quartz plate (1×2 cm^2). SEM images show that when the concentrations of BFTA solution is

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low (1×10^{-3} M), only random nano/micro particles with various sizes could be observed. And while the concentration is increased to 1×10^{-1} M, lots of big agglomeration formed (Fig S1). Both the above films are unfavourable for solid sensing considering their poor surface area. Fig. 2 shows representative SEM images of BFTA films with a concentration of 1×10^{-2} M. At this concentration, a large area of continuous and highly wrinkled film formed. Such surface morphology is helpful for enhancing the contact probability between the sensing film and the anylates due to its larger surface area. So the concentration of 1×10^{-2} M is adopted for the optimized film preparation conditions. We reasoned that when the films contact with primary amine or secondary amine, corresponding imine or phenol should appear leading to changes in both absorption and emission spectra.

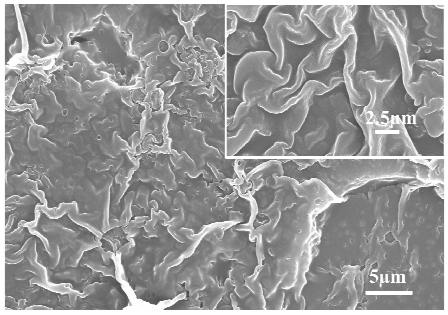

Fig. 2 SEM images of BFTA films by spin-coating its THF solution (1×10^{-2} M) on the quartz plate (1×2 cm^2). Inset: Magnified SEM image of BFTA films.

Firstly, we investigate the absorption spectra changes upon exposure to saturated vapours of primary amine (including primary aliphatic amine and primary aromatic amine) and secondary amine for 5 minutes (Fig. 3a). The final maximum absorption peaks experienced different shift with $\Delta\lambda_{max}$ of -4 nm, -5 nm, -1nm, 29 nm, 22 nm and 22 nm for *n*-propylamine, *n*-hexylamine, benzylamine, aniline, diethylamine and diisopropylamine, respectively. Obviously, the spectra changes showed some regularity: (a) The spectra undergo a little blue shift for the primary aliphatic amines such as propylamine, hexylamine and benzylamine; (b) in contrast, the spectra undergo distinct red shifts in the primary aromatic amine such as aniline and the secondary amine including diethylamine and diisopropylamine. This can be deduced by the structures of the final products of BFTA after exposure to different amines: (a) For the primary aliphatic amines, the final product is imine containing aliphatic chain, thus the effective conjugation length did not change much compared to the foremost aldehyde group, resulting in the minor change in UV-vis spectra; (b) In contrast, for primary aromatic amines, the final product is aromatic imine with the extended conjugation length compared to the foremost aldehyde group, leading to a red-shift in the spectra; (c) In the presence of secondary amine vapour, the phenyl boronate ester group was converted to phenol. Thus the initial intramolecular charge transfer (ICT) from phenyl boronate ester to aldehyde became into one from phenol to aldehyde. The electron-donating capability of phenol is stronger than that of phenyl boronate ester bringing more efficient intramolecular charge transfer and resulting in a red-shift in the spectra.

Compared with those of UV-Vis spectra, the changes of the fluorescent spectra before and after exposure in diversiform amines were even more diverse (Fig. 3b). Almost each primary amine corresponds to a specific emission spectrum. In order to further explore this phenomenon, we separated the actual products after exposure to these amines and characterized them with ^{1}HNMR spectra and the high resolution mass spectrum (HR-MS) (see Supporting Information). As expected, the final products were all confirmed to be the corresponding Schiff bases

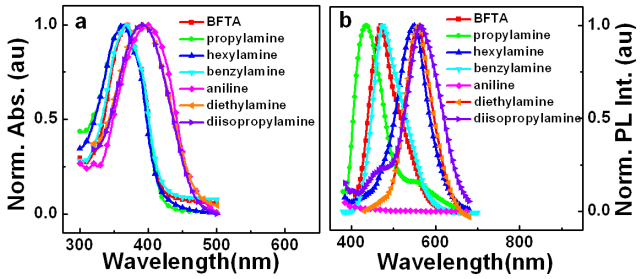

Fig. 3 The normalized Uv-vis spectra (a) and fluorescence spectra (b) of BFTA films in the presence of different saturated amines vapour.

with high yields after sufficient exposure in *n*-propylamine, *n*-hexylamine, benzylamine and aniline. For example, in saturated aniline vapour , the final product is (*E*)-*N*-((5-(9,9-dioctyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-2-yl)thiophen-2-yl)methylene)benzenamine. Usually, the aromatic Schiff base has a low fluorescent quantum yield due to an efficient process of photoinduced electron transfer (PET) from the fluorophore to the aromatic imine. [18] This nicely explained why the fluorescence of the BFTA film was quenched quickly after exposed to aniline vapour. Whereas in the primary aliphatic amines, the PET process in the new formed aliphatic imines molecules was not strong enough to quench the fluorescence. Hereby, the fluoresce spectra of BFTA in the primary aliphatic amines shifted accordingly with the change of the imines backbone. For example, the maximum emission peak blue shifted from 470 nm to 435 nm after exposure to *n*-propylamine. In presence of *n*-hexylamine and benzylamine, the maximum emission peaks red-shifted from 470 nm to 548nm and 475 nm, respectively. Different with the case for primary amine, for secondary amine such as diethylamine and diispropylamine, the final reaction products were both 5-(2-hydroxy-9, -dioctyl-9H-fluoren-7-yl) thiophene-2-carbaldehyde. Accordingly, their fluorescence emission spectra are all shifted to around -560 nm.

To further understand the variation of spectra, the electron distributions of the HOMO and LUMO energy level of BFTA and corresponding Schiff-base/ phenol products are calculated (Fig S2). All the theoretical calculation was accomplished by using density functional theory (DFT) with DMol^3 code provided by the Materials Studio package.[19] Comparison of the electron distribution in the frontier MOS of these compounds illuminates that a slight change in the structure of the compound may induce an obvious change in electron density and the ICT behavior. This result, to some extent, can explain why the imines with similar structures present different fluorescence. Besides, other factors, such as the nucleophilicity of amine, the steric hindrance of the alkyl chains and the lipophilicity of amine could also influence the fluorescent spectra. [20]

The huge change in the fluorescence spectra could also be reflected by changes of fluorescence color. As shown in Fig. 4a, the BFTA films undergo significant changes in emission color upon exposed to different amines with a colorful fluorescence

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including pink, green, yellow and orange. Such changes can be readily distinguished by naked eyes. To describe these fluorescence colors accurately, we take advantage of the CIE system of colorimetry which has been successfully used in ECD system to distinguish them. The CIE 1931 color coordinates were acquired according to the relevant fluorescent spectra with the values to be (0.16, 0.23) in air, (0.19, 0.14) in *n*-propylamine, (0.33, 0.53) in *n*-hexylamine, (0.16, 0.29) in benzylamine, (0.40, 0.56) in diethylamine and (0.41, 0.46) in diispropylamine.The color coordinate for the aniline exposure film could not be calculated owing to its very weak fluorescence. With the excellent color-matching between the fluorescence and the CIE chromaticity diagram, vapours with similar structures could be further distinguished (Fig. 4b).

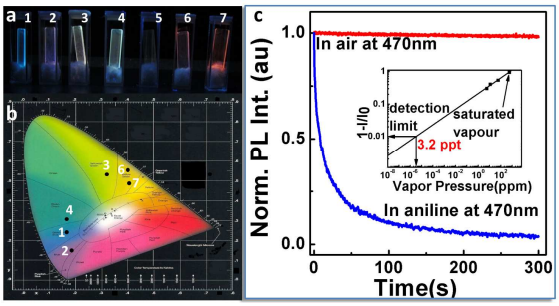

Fig. 4 a) BFTA films excited by UV lamp 365 nm after 300 S' exposure in air and several saturated organic amine vapour (1 air 2 *n*-propylamine 3 *n*-hexylamine 4 benzylamine 5 aniline 6 diethylamine 7 diisopropylamine). b) CIE 1931(x, y) chromaticity diagram of the films in the above saturated vapours of different amines.c) Changes in fluorescence intensity of BFTA 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.

Photo stability, response time and sensitivity are key factors for the evaluation of a probe. As shown in Fig. 4c, the emission intensity of the BFTA film at 470 nm was monitored upon continuous UV-excitation for 300 s in air. The almost unbleached emission indicates its high photo-stability. Further experimental data show the fluorescence intensity of the film keeps almost unchanged after exposure to air for one month. Upon exposure to saturated aniline vapour, its fluorescence was quenched by 54 %, 87 % and 96 % within 10 s, 50 s and 300 s, respectively, which indicated its high sensitivity and fast response to aniline vapour. Theoretically, except for aniline, other amine could all be detected at dual- or multi- wavelength because their output signal is based on the shift of fluorescent spectra. Indeed, with the disappearance of the BFTA and the appearance of corresponding converted products, the fluorescence intensity changes at dual wavelength were factually recorded through both a turn-off mode and a turn-on mode in different amines vapour except for aniline vapour. (Fig. S3-Fig.S8). To estimate the detection limit of this probe for different amines, we measured the changes in fluorescence intensity of BFTA films when exposed to each amine vapour with at least four different concentrations (picked from the vapour of 1, 10, 25, 50 and 100 times diluted from their each saturated vapour). And the intensity quenching data ($1-I/I_0$) are well-fitted to the Langmuir equation with an assumption that the quenching efficiency is proportional to the surface adsorption of amine vapour (Fig. S9-Fig. S14). If the signal-to-noise ratio of the fluorescence detection device was considered as 1%, the detection limits of BFTA can be estimated to be ppm ~ ppt level (Table S1). The detection limits of this probe to different amines are far below their IDLH (Immediately Dangerous to Life or Health) 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. Further experiments confirmed that the detection limits at wavelength of 470 nm are more sensitive for these amines compared to detection at other wavelength.

In summary, this study demonstrates the first example utilizing a single fluorescent probe for a simultaneous detection of multifarious amines in multicolor imaging. The probe exhibits excellent sensitivity, nice selectivity and fast response. Compared with other reported probes for amine vapour sensing, the presented probe possesses the following advantages: a) This multi-reaction-spots molecule could generate corresponding response to different analyte vapour according to their specific reaction activity; b) Unlike other reactive fluorescent probes applied in the solution systems, such solid-state reactive probe has high conversion rate and conversion efficiency with response time in seconds and detection limits as low as ~ppt levels. This work offers a new strategy for designing intelligent materials to identify multiple anylates in films simultaneously. Endeavors to further modification of the sensory materials so as to differentiate other important species are underway in our laboratory.

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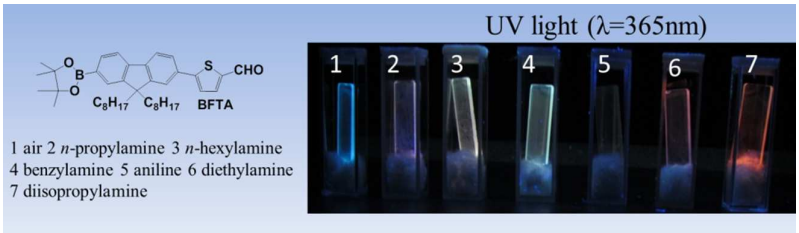

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