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ARTICLE TYPE

Reversible and "fingerprint" fluorescence differentiation of different organic amines vapours using a single conjugated polymer probe

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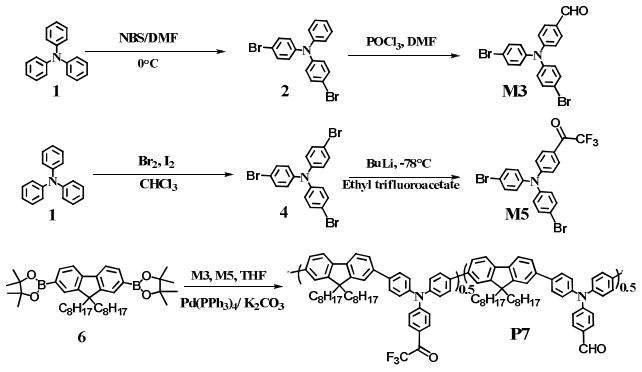
By embedding multiple reactive groups onto one conjugated polymer backbone, an ultrasensitive and reversible "fingerprint" fluorescent probe for simultaneous detection of primary aliphatic amine, secondary aliphatic amine as well as aromatic amine and their mixture has been reported.

The development of selective and sensitive fluorescent probes for detecting vapour phase analyte has always been a challenging task in molecular recognition research because of the scarcity of smart material which can bind anylate through strong interaction in the solid state[1]. Particularly, a single probe which can distinguish multiple anylate simultaneously is scarce[2]. In the past, the detection of multiple anylates with similar structures was usually performed by an optical detecting array in spite of its disadvantage such as large location error, cross talk and large invasive effect[3]. Therefore, there are still in great need of ingenious strategies for monitoring multi-analyte selectively on-site via a simple probe without complicated preparing procedure[4].

It is of great importance to detect trace volatile organic amines in air due to their high toxicity to human health as well as the potential risk to the environment[5]. A single probe which can distinguish the type of organic amine (such as primary amine, secondary amine as well as tertiary amine) is highly desired because the recognition has virtual significance in practical applications[6]. This contribution is partially inspired by our recent research on the simultaneously detecting different amines vapour by combing multiple reactive groups into one small molecule[7]. Despite notable successes in identifying different amines, the reported probe is irreversible which limit its further use. Furthermore, the sensing behavior may become complicated when multiple amines are present together. The objective of this contribution is to solve these two problems and prepare selective, reversible, and ultrasensitive fluorescent probe for organic amines vapour detection.

To design such a probe, suitable functional groups should be chosen. Herein, the aldehyde group, a famous group which can selectively bind with primary amine through Schiff base reaction, is chosen to identify primary amine. Trifluoroacetyl group is another good reactive unit which can reversibly react with organic amines to afford hemiaminals or zwitterions. Although Mohr et al. have reported lots of receptors based on this group to selectively detect aliphatic amines, there still remains much scope to be improved[8]. For example, most sensors reported by them merely showed high sensitivity to primary aliphatic amines[9]. Moreover the detection for amines was mostly conducted in solution[10]. Hereon, we attempt to incorporate the reactive units of aldehyde and trifluoroacetyl into one probe for the selective amine vapour sensing in solid state.

Compared to small molecule, conjugated polymer has many advantages in film sensing: (a) Conjugated polymer has much higher sensitivity than corresponding small molecule due to the molecule wire effect [11]; (b) The presence of conjugated backbone can decrease self-aggregation of the sensory material and improve the film-forming properties; (c) By combination of a variety of functional groups into a conjugated polymer, the electron could delocalized on the whole chain and present the cooperative effects, which will result in more versatile signal change. Considering all these factors, in this work, we constructed a new type of conjugated "reactive" polymer probe (**Scheme 1**) for multiplate amine vapour detection.



Scheme 1. Preparation of **M3**, **M5** and **P7**

The monomers **M3** and **M5** as well as polymer **P7** were prepared according to the synthetic route shown in **Scheme 1**. Polymer **P7** was prepared by copolymerization of **M3**, **M5** and compound **6** through Suzuki coupling reaction in high yield (76%). All **M3**, **M5** and **P7** show considerable fluorescence both in solutions and in films. The fluorescence quantum yields of **M3**, **M5** and **P7** are estimated to be 0.46, 0.21 and 0.24 measured in solution using 9, 10-diphenylanthracene as reference and their

optical spectra in solution were shown in **Fig. S1**.

The absorption and emission spectra of **M3**, **M5** and **P7** in films were illustrated in **Fig. 1a**. The maximum absorption peaks of **M3**, **M5** and **P7** are located at 373 nm, 394 nm and 414 nm, receptively, indicating an expanded conjugation in **P7** backbone. And their maximum emission peaks are 461 nm, 509 nm and 525 nm, receptively, corresponding to the fluorescence of blue, green

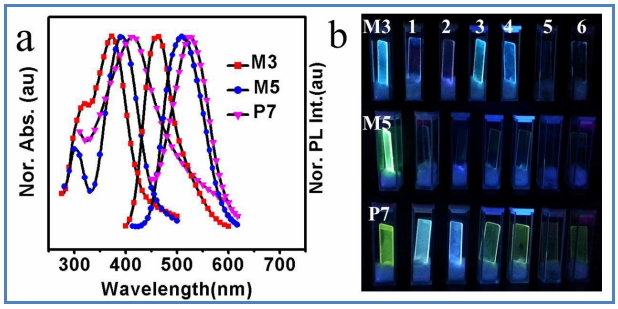


Fig. 1. (a) Normalized absorption and fluorescence spectra of **M3**, **M5** and **P7** films. (b) Films of **M3**，**M5** and **P7** excited by UV lamp 365 nm after 300S's exposure to air and several other saturated organic amine vapour (1 **PA** 2 **HA** 3 **DEA** 4 **DPA** 5 **AN** 6 **TN**).

and yellow. To compare their sensing potential to different kinds of amines intuitively, the sensing films made of **M3**, **M5** and **P7** were prepared by spin-coating method and then put into the saturated vapour of different amines. Here, two representative amines for each kind of amines including primary aliphatic amine [*n*-propylamine (**PA**) and *n*-hexylamine (**HA**)], secondary aliphatic amine [diethylamine (**DEA**) and dipropylamine (**DPA**)] and aromatic amine [aniline (**AN**) and *o*-toluidine (**TN**)] were selected. As shown in **Fig. 1b**, **M3** films only respond to primary aliphatic amine and aromatic amine via Schiff base reaction with them. But in presence of secondary amines, the fluorescence of **M3** shows no obvious change. As comparison, the fluorescence of **M5** films was all quenched in these amines for the hemiaminals formation. Therefore, both **M3** and **M5** lack enough selectivity to these amines. As for **P7** films, it can respond to and differentiate these three types amines with emission color change or fluorescence quenching by a cooperative effects of the two reactive functional groups. Obviously, **P7** shows considerable selectivity to these three kinds of amine vapour.

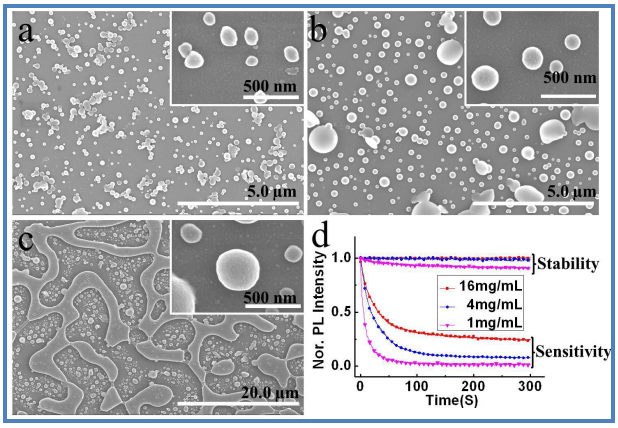


Fig. 2. SEM images of **P7** films made by spin-coating method with its THF solutions of different concentrations (a) 1mg/mL, (b) 4mg/mL and (c) 16mg/mL. Inset: Magnified SEM image of films. (d) Changes in fluorescence intensity of **P7** films after exposure to air and saturated **AN** vapour for 300 s at 20 °C at their maximum emission wavelength.

For solid state fluorescence sensing, the surface morphology of film plays key role in the sensing performance. Herein, we prepared **P7** films via a concentration control and compared their surface morphology, photo stability and sensitivity to **AN** vapour. As shown in **Fig. 2a** and **2b**, when the concentration of **P7** is dilute, it tends to form nanospheres on the quartz plate. Moreover, with the increase of concentrations, the nanosphere will gradually grow. For example, the diameters of nanosphere change from ~110-160 nm to ~130-250 nm when the concentration is elevated from 1 mg/mL to 4 mg/mL. A further concentration increase to 16 mg/mL lead to larger nanospheres and some will stick together to form almost continuous band structure with varied width as **Fig. 2c** shows.

Fig. 2d indicates that the photo bleaching of the **P7** films made from the solution with concentration of 1 mg/mL, 4 mg/mL and 16 mg/mL, respectively, are about 5 %, 1% and 0.5 % upon continuous excitation within 300 s. It means the more concentrated the solution is, the better optical stability the film made of this solution has. Contrary to the photostability, upon exposure to **AN** vapour, corresponding fluorescence quenching of **P7** films are 98%, 93% and 76%, respectively. This can be easily interpreted that the smaller size of the nanoparticle is related to higher specific surface area which is more favorable for vapour sensing. Considering the two factors of sensitivity and photo stability, we selected 4 mg/mL as the optimal preparation conditions for **P7** films.

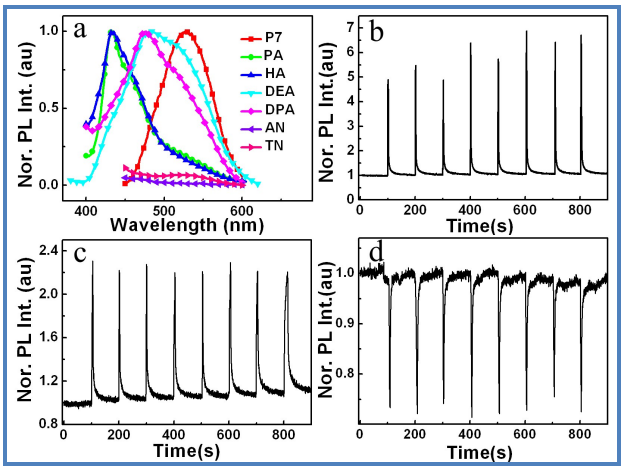


Fig. 3. (a) The normalized fluorescence spectra of **P7** films in presence of different saturated amines vapour. (b) Time resolved fluorescence intensity of **P7** film at 435nm upon consecutive exposure to saturated **PA** vapour. (c) Time resolved fluorescence intensity of **P7** film at 475nm upon consecutive exposure to saturated **DPA** vapour. (d) Time resolved fluorescence intensity of **P7** film at 525nm upon consecutive exposure to saturated **AN** vapour.

As mentioned above, the **P7** films present good selectivity to primary aliphatic amine, secondary aliphatic amine and aromatic amine with three kinds of completely different fluorescence changes. Such huge changes are also reflected by fluorescence spectra. As shown in **Fig. 3a**, upon exposure to the primary amines vapour, the emission maximum of **P7** blue shifted from

525 nm to 435 nm. And in secondary amine, the emission maximum blue shifted to ~475 nm. While in aromatic amines, the emission at 525 nm is almost completely quenched. As designed, in primary alkyl and aromatic amines, both aldehyde and trifluoroacetyl groups are involved in the reactions, while only trifluoroacetyl group reacted with secondary mines. Among them, the new formed aromatic imine group naturally has a low fluorescent quantum yield because of an efficient intramolecular photoinduced electron transfer process [12]. Thus the fluorescence is quenched by aromatic amines but blue shifted in primary aliphatic amine. All experimental data support that each kind of amine corresponds to a special detection wavelength like "fingerprint" with the occurrence of one emission peak at 435 nm for primary aliphatic amine, 475 nm for secondary aliphatic amine, and a fluorescence quenching at 525 nm for aromatic amine.

The reversibility of this probe was tested via monitoring the emission intensity change at 435 nm upon repeated exposure to saturated **PA** vapour within very short time (less than 2 s). As revealed in **Fig. 3b**, Even after repeated exposure for eight times, the fluorescence intensity is still very stable compared with its initial fluorescence demonstrating an excellent reversibility, which is advantageous for quick and long time on-spot use in amine detection. Similar experimental results were recorded when detecting **DPA** at 475 nm and detecting **AN** at 525 nm (**Fig. 3c**, **Fig. 3d**).

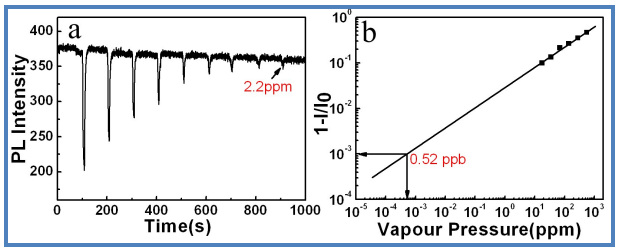


Fig. 4. (a) Time-course fluorescence responses of P7 films at 525nm to the different concentration of **AN** vapor: First exposure was 560 ppm, the next exposure was at half-diluted concentration of the front vapor. (b) Fluorescence quenching efficiency ($1-I/I_0$) as a function of the vapour pressure of **AN** at 525nm: data (error ± 5%) fitted with the Langmuir equation.

Table 1. Saturated vapour pressure of different amines at 20 °C (KPa) and the experimentally determined detection limits of **P7** for relevant volatile amines.

Anylate	SP[a]	DL[b]	IDLH[c] [ppm]
PA	33.0[d]	114 ppm	—
HA	0.89[e]	4.0 ppm	—
DEA	25.11[e]	190 ppm	200
DPA	2.39[e]	0.036 ppb	—
AN	0.056[e]	0.52 ppb	100
TN	0.015[e]	0.55 ppt	50

[a] Saturated vapour pressure at 20 °C/KPa [b] Detection limit [c] IDLH is an acronym for Immediately Dangerous to Life or Health [d] From Wikipedia, the free encyclopedia [e] Calculated through Antoine equation according to the data from the Lange's Hand book of Chemistry and the CRC Handbook

Sensitivity is another key factor to evaluate a probe. **Fig. 4a** shows the transient fluorescent changes of P7 upon consecutive exposures of **P7** to various concentrations of **AN** vapour within very short time (less 2 s). The result reveals that the **AN** vapour can be directly detected even at ultra-low concentration as low as 2.2 ppm. The detection limits for these amines were extrapolated according to their fitted plot (**Fig. 4b**, **Fig. S2- Fig S6**) and were shown in **Table 1**. The detection limits of this probe to different amines are all below their IDLH (Immediately Dangerous to Life or Health) concentrations. For example, the detection limit for **TN** can be as low as ~0.55 ppt which is much lower than its IDLH concentration of 50 ppm.

To further demonstrate the selectivity of this probe, several common organic solvents including dichloromethane, tetrahydrofuran, acetone, water and ethyl acetate were selected as interference reagents and the interaction of the probe with these solvents were investigated. No obvious fluorescence intensity change (less than 3%) was observed upon exposure to these vapours indicating the sensing film demonstrates excellent selectivity towards organic amines. In addition, in presence of tertiary amine such as triethylamine, no distinguishable change could be detected for its fluorescence by naked eyes. And the emission maximum keeps almost unchanged with a slightly wider spectrum (**Fig. S7**).

In order to test the performance of the probe in very complicated environment, we also investigate the emission spectra change of **P7** under a mixture vapour of these six amines. As shown in **Fig. S8**, the resulting spectra are actually the superimposed spectra of independent **P7** film reacting with each amine. Fortunately, primary aliphatic amine, secondary aliphatic amine and aromatic amine can all be easily differentiated and reversibly detected by their *fingerprint* signals at 435, 475 and 525 nm (**Fig. S9**). It indicates that **P7** is not only suitable for qualitative detection of individual vapour but also for mixture vapour of different amine.

In conclusion, by incorporating multi-reaction sites onto one conjugated polymer chain, we have developed a fluorescent conjugated polymer probe which can realize a fingerprint fluorescence detection of different amine vapours and their mixture with excellent reversibility, short response time and high sensitivity (even 0.55 ppt). This work offers a smart strategy for the design of highly efficient fluorescent probe for a simultaneous detection of multiple anylates. Endeavors to further modification of the sensory materials so as to differentiate more amines such as tertiary amine are underway in our laboratory.

Acknowledgment

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Notes and references

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