A mild and catalyst-free conversion of solid phase benzylidenemalononitrile/benzylidenemalonate to N-benzylidene-amine and its application for fluorescence detection of primary alkyl amine vapor†

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A new rapid and catalyst-free solid/vapor reaction between benzylidenemalononitrile/benzylidenemalonate and primary alkyl amines was found. With these as sensory units of fluorescent polymers, probes for primary amine vapor with high sensitivity and selectivity were developed.

As important intermediates in chemical industry, amines such as amphetamine derivatives have received great attention for use in chemical leakage, food security and drug abuse. Methods for detection of amines have been developed using electrochemistry,1,2 chromatography3 and colorimetry.4–7 Fluorescent sensors could be easily integrated as very sensitive portable devices for real-time vapor-phase detection, which have been attracting broad interest these days. Vapor detection of amines by fluorescence methods has been reported via bonding interaction8–10 and photoinduced electron transfer.11,12 However, many sensory materials tend to respond to all kinds of amines.13 Our group developed some methods for detection of secondary amines (for example methamphetamine) and aniline with high sensitivity and selectivity.14 But until now, no study has been reported that could efficiently differentiate the primary amines from secondary and tertiary amines by a specific chemical reaction.10 To solve the problem, two aspects will be highly favorable especially for in situ detection. On the one hand, developing a reaction with high specificity within a very short reaction time and under mild conditions will be highly preferred especially for in situ detection. On the other hand, for fluorescence detection, a molecular wire effect and a large spectral change will be favored for sensitive detection, which will be advantageous for the detection by preventing the background noise interference.

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In this work, one unusual reaction between the benzylidenemalonate (BZMA)/benzylidenemalononitrile (BZMN) derivative solid film and primary amine vapor was found. Within five minutes, BZMA/BZMN could be converted to benzylidene-propylamine without any catalyst (Fig. 1) at room temperature. With these two units as the sensing units, fluorescent conjugated copolymers were designed and synthesized for primary amine vapor sensing. The sensing behavior was investigated systematically (Fig. 1).

The reaction was found accidentally when the drop-casted film of dibromophenylamino-benzylidenemalonate (M1) was put aside in an atmosphere of n-propylamine vapor. 5 min later, the color of the film changed from bright yellow to pale yellow, and the emission color changed from green to bluish-green. To determine the reason behind this phenomenon, the amine exposed film was vacuum dried to remove the volatile compounds, then the 1H-NMR spectrum of the film species dissolved in CDCl3 was recorded. It is observed that the peak attributed to the ethyl units on the ester disappeared with the formation of new n-propyl-groups, which is different from that of n-propylamine, and the characteristic singlet peak of a proton located on ethylene shifted from 7.6 to 8.1 ppm reflecting a different conjugation that reduced the electron density on this H-atom (Fig. 2). The high resolution mass spectrum (HR-MS) exhibits a molecular ion peak at 469.9995, which combined with the 13C-NMR (Fig. S3, ESI†) results proved the formation of the N-benzylidened-propylamine structure. It is found that only primary alkyl amines could react with M1. Other amines including secondary amines, tertiary amines or aniline derivatives were tested and no interaction
was found between the secondary amines, tertiary amines or aniline derivatives and M1 under the same conditions within 30 minutes (Table S2, ESI†).

More interestingly, the same phenomenon was found when M1 was replaced by dibromophenyl-aminobenzylidenemalononitrile (M2). Upon exposure to n-propylamine, the color of the film changed from brown-red to pale yellow, and the emission color changed from orange to bluish-green. Similarly, M2 could also only react selectively with primary alkyl amines but could not react with secondary, tertiary and aromatic amines. The identical 1H-NMR and 13C-NMR data were observed as that of M1. HRMS results further confirm that the same product was produced. It was really unexpected that the carbon–carbon double bonds linked with diester or dicyno units were broken to form such carbon–nitrogen double bonds of Schiff’s base upon exposure to primary amine vapor under such mild conditions. Such reactions usually occur in different ways15,16 and should be conducted in solution in the presence of a catalyst and/or under heating conditions in addition to longer reaction time. The proposed reaction mechanism is presented in Fig. S2 (ESI†). At present, the detailed mechanism of C==C breakage and the formation of C==N is still unknown.

Actually, for both M1 and M2, there exists intramolecular charge transfer (ICT) with triphenylamines as electron-donors, and malonates or malononitriles as electron-acceptors. But after the reaction with primary amines, malonates or malononitriles were converted to N-benzylidene-propylamine, which significantly decreased the electron-withdrawing capacity of the acceptors. Such a larger ICT change means a large emission change, which could be used for primary amine probe design. Therefore, if M1 or M2 could be used as sensing units to construct a fluorescent conjugated polymer probe, it will result in a greater fluorescence signal change and higher sensitivity due to the molecular wire effect. Therefore, probe P1/P2 were designed and synthesized by alternative copolymerization of M1/M2 with the fluorene unit via a palladium catalyzed Suzuki coupling reaction (Scheme 1). The synthesis of the polymers and the characterization data are provided in the ESL†, with no malonate or malononitrile units, was also synthesized for comparison. In addition, the reason to choose the fluorene unit is its well known highly efficient fluorescence and stability.

Both P1 and P2 tend to form a porous film on a quartz substrate by drop-casting its toluene solution onto the quartz surface after evaporation of a natural solvent, which was observed by SEM (Fig. 3). The bright area is the polymer, and the dark region is the substrate. Such a surface morphology led to enhanced gas permeability and a large surface area to volume ratio, which are advantageous for vapor-phase sensing. In comparison, under the same conditions, no such porous film could be found for P0, indicating that BZMA/BZMN units are critical for the formation of the porous structure.

P1 showed maximum emission at 531 nm corresponding to yellowish-green fluorescence and P2 showed maximum emission at 573 nm corresponding to orange fluorescence (Fig. S1 and Table S1, ESI†). Stokes shifts of P1 and P2 are at 151 and 197 nm (52 nm for P0), respectively. A larger Stokes shift could greatly improve the sensitivity to trace quantities of analytes because of its larger signal-to-noise ratio and low self-absorption.

To investigate the sensory character of P1 and P2 films, we tested the changes in emission spectra and time-course fluorescence response in benzylamine (BZA) vapor. BZA was selected because of its relatively low saturated vapor pressure (672 ppm, 15 °C),17 and it could be easily diluted and also prevents the liquefaction on polymer films. As shown in Fig. 4, the emission was...
peak of P1 at 531 nm blue-shifted to 522 nm and the maximum intensity increased by 45% upon exposure to saturated BZA vapor for 300 s. In comparison, the emission peak of P2 at 573 nm blue-shifted to 522 nm and achieved a 7-fold enhanced emission signal at this wavelength. P2 experienced a much larger emission peak shift, and the emission color changed from orange to bluish-green, while that of P1 transformed from green to bluish-green (Fig. 4). The bigger emission wavelength and intensity change could be easily detected by the naked eye (Fig. S4, ESI†) either under sunlight or UV irradiation, which means P2 would be a much better probe for primary amine vapor sensing.

Since saturated BZA vapor could trigger a very fast emission change from P2 to the resulting polymer with Schiff's base units, to monitor the reaction kinetics between the amine and malononitrile groups, the concentration of BZA was further diluted to 100 ppm. As expected, upon exposure to BZA vapor, the emission peak at 573 nm steadily decreased and blue shifted while a new peak appeared at around 425 nm [Fig. 5a]; finally it was completely converted to the emission band peaked at 522 nm as shown in Fig. 4, reflecting the kinetics of the chemical change. The emission decrease reflects the breaking of the C–C bond between TPA and malononitrile, and the steadily blue-shifted peak is attributed to the superposition of the emission spectrum of P2 and the newly formed polymer. As mentioned above, the formation of Schiff's base greatly decreases the electron-withdrawing ability of the acceptor, which results in a much blue-shifted emission. It is worth mentioning that under such a low vapor pressure, it will take quite a long time to be fully converted to the resulting polymer. Further diluted vapor samples were prepared to test the sensitivity. The emission intensity at 480 nm was increased by 230%, 70% and 20% upon exposure to 200 ppm, 100 ppm and 50 ppm benzylamine vapor for 300 s (Fig. 5b). Herein, the detection limit for BZA is calculated to be 30 ppm (Fig. S5, ESI†).

Considering that ICT-type fluorescent materials tend to change their emission wavelength in different polar environments, the selectivity of the probe film was further checked to avoid the influence of solvatochromism or vaporchromism caused by swelling and liquefying of common volatile organic solvents. It is found that common solvents, such as THF, acetone, toluene, alcohol and chloroform, all cause reversible fluorescent quenching. Since the fluorescence response of the sensory polymer adopts a fluorescence turn-on mode, it could be easily differentiated from other interference substances, in other words, it demonstrated nice selectivity.

A highly efficient new solid/vapor reaction between BZMA/BZMN and primary alkyl amines under catalyst free and mild conditions was found. Two fluorescent copolymer probes for primary amine vapor sensing were constructed using the two units as sensing units. Both polymers tend to form a porous film, which is beneficial for vapor penetration. The polymer with BZMN could trigger a much bigger emission wavelength change (from orange to bluish-green). The fluorescence spectra change at low concentration of BZA vapor clearly presented the chemical reaction kinetics. The special solid/vapor reaction that triggered large spectrum-shift and fluorescence turn-on detection represents an efficient way for the design of a highly sensitive and selective fluorescent sensor. And a highly efficient catalyst-free solid/vapor phase reaction also provided a green and economic way to synthesize such Schiff's base compounds.

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Notes and references

17 The vapor pressure data are cited from CRC handbook of Chemistry and Physics, CRC Press, 90th edn, 2010, VAPOR PRESSURE.