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A selective fluorescence turn-on sensor for trace vapor detection of hydrogen peroxide†

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A fluorescence turn-on sensor molecule (C6NIB) has been synthesized and fabricated into a porous matrix to enable trace vapor detection of hydrogen peroxide. The detection limit was projected to be below 5 ppb.

Among the explosive detection methods developed thus far, vapor detection represents a non-destructive way suited for both trace and bulk explosive monitoring.[1] For vapor detection, fluorescent sensing represents a simple, rapid, and highly sensitive technology.[1a–g] Recently, fluorescence "turn-on" (or enhancement) molecular sensors have drawn increasing attention for explosive detection,[1g,2] as the detection sensitivity is improved due to the low (ideally zero) fluorescent background of the pristine state of sensors.

Triacetone triperoxide (TATP), along with other peroxide explosives such as diacetone diperoxide (DADP) and hexamethylene triperoxide diamine (HMTD), represent one class of the most elusive explosives that can be easily made at home from commercially available precursors. These peroxide explosives are difficult to detect by conventional analytical techniques due to their lack of a nitro group, non-fluorescence, low ionizability and minimal UV-vis absorption.[3] Hydrogen peroxide (H_2O_2) is usually considered as a signature compound for detecting peroxide explosives,[3a,4] from which H_2O_2 can be produced through UV decomposition or simply leaking as an intrinsic impurity. Moreover, liquid mixtures of concentrated hydrogen peroxide and fuels (*e.g.*, alcohols and acetone) can be used as powerful explosives as well. Thereby, expedient trace vapor detection of H_2O_2 becomes critical for these security scenarios.[2e]

Although various methods and technologies have been developed to detect H_2O_2, such as the electrochemical method,[5] colorimetric[6] and fluorimetric method,[1g,2b,d,7] vapor detection of H_2O_2 (particularly at the trace level, *e.g.* ppb) still remains challenging. This is mainly due to the combined difficulty of molecular design and materials engineering to produce a sensor system that enables not only strong binding with H_2O_2 (for efficient vapor sampling), but also an expedient, selective reaction with H_2O_2 to transduce the readable signal. While a few recent papers reported on fluorescence turn-on sensors that can be employed for vapor detection of H_2O_2,[1g,2b] the reported sensors either suffer from long response time (>10 min) or complicated instrument alignment (*e.g.* involving laser and cooled CCD). There is a great need to develop a simple, expedient fluorescence turn-on sensor system that can detect H_2O_2 vapor, ideally down to a level of ppb.

Inspired by the recent studies on the molecular design of naphthalimide based robust fluorescence turn-on sensors,[8] we report herein on a new fluorescence turn-on sensor for H_2O_2, 2-hexyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-benzo-[de]isoquinoline-1,3(2*H*)-dione (C6NIB). This molecule is only weakly fluorescent in the UV region (λ_{max} at 392 nm) mainly caused by the π–π⋆ transition of the naphthalimide backbone (Fig. S1, ESI†), for which the quantum yield is only 0.6% under basic conditions as employed for the sensor in this study. However, upon reaction with H_2O_2 the aryl boronate group of C6NIB is transformed to phenol (Fig. 1a), forming an electron donor–acceptor (push–pull) structure that turns on the charge transfer transition. As shown in Fig. 2a, the main absorption peak of the oxidation product, 2-hexyl-6-hydroxy-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione (C6NIO), shifts to the red by *ca.* 90 nm. The new absorption band at the longer wavelength region corresponds to the intramolecular charge transfer (ICT) transition between the phenol and naphthalimide groups.[8,9] Before the addition of H_2O_2, the ethanol solution of C6NIB exhibited no detectable emission in the ICT band, whereas strong emission was observed in the presence of H_2O_2 (Fig. 2b). Such a fluorescence turn-on reaction is intrinsically selective for H_2O_2, with no fluorescence increase observed in the presence of water, oxygen, or common organic reagents such as alcohols, hexane, acetone, *etc.* (Fig. 1b). The high selectivity is due to the specific chemical reaction between the boronate group and H_2O_2, which has been proven by previous studies in solutions, whereas the boronate molecules are based on different backbone structures.[7c]

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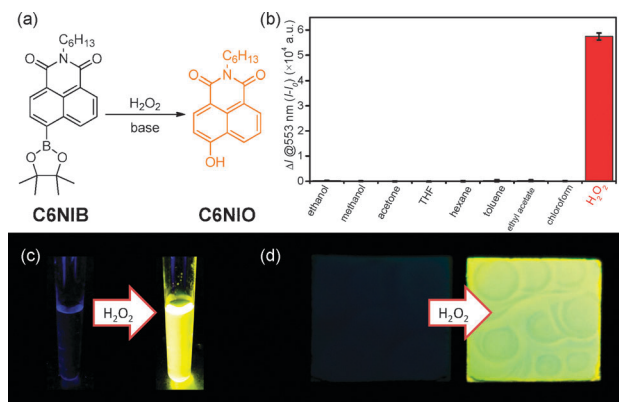
Fig. 1 (a) The fluorescence turn-on reaction between the sensor molecule (C6NIB) and H_2O_2. (b) The sensing of C6NIB is extremely selective for H_2O_2 (225 ppm) as tested against the saturated vapor of other common solvents, ethanol (89 000 ppm), methanol (131 000 ppm), acetone (260 000 ppm), THF (173 000 ppm), hexane (130 000 ppm), toluene (26 000 ppm), ethyl acetate (100 000 ppm), chloroform (140 000 ppm). (c and d) Photographs showing the fluorescence turn-on of C6NIB in an ethanol solution (1×10^{-3} mol L^{-1}, containing 1×10^{-2} mol L^{-1} TBAH) and dispersed in a 1.5×1.5 cm^2 silica gel TLC plate (0.5 μmol C6NIB and 5 μmol TBAH) after exposure to H_2O_2.
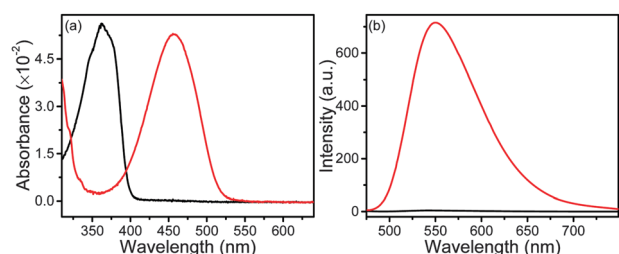

Fig. 2 (a) Absorption and (b) fluorescence spectra of an ethanol solution of C6NIB (5×10^{-6} mol L^{-1}, in the presence of 5×10^{-4} mol L^{-1} TBAH) before (black) and after (red) addition of 5×10^{-3} mol L^{-1} H_2O_2.

The high chemical selectivity, together with the high fluorescence turn-on sensitivity, makes C6NIB an ideal sensor for vapor detection of H_2O_2, for which fast response and low detection limit are the two critical goals to be approached through materials engineering. The presence of the boronate group makes the C6NIB molecule highly hydrophilic, thus suited for blending with hydrophilic porous materials such as silica gel (Fig. 1d). The composite sensory material thus fabricated possesses large surface area, continuous porosity and a hydrophilic interface, which enhance the absorption of H_2O_2 vapor.

Molecular design and synthesis of C6NIB represents an advancement in the development of boronate sensors. Direct attachment of the boronate group to an electron deficient aromatic system is challenging, even through the efficient Miyaura boration reaction.[10] Indeed, only a few studies have been reported on the manipulation of the "push–pull" electronic structure of the naphthalimide backbone by direct attachment of an electron deficient group.[8b,11] Nonetheless, once the molecule is modified with an electron deficient group like boronate, it will become a strong electrophile with increasing reactivity with H_2O_2.

The H_2O_2-mediated oxidation of aryl boronates is kinetically favored under basic conditions, which facilitates the dissociation of H_2O_2 into the HO_2^- anion (acting as a nucleophile) that can in turn react with the boronate group (a strong electrophile).[7c] Moreover, under basic conditions the phenol group of C6NIO undergoes deprotonation, becoming phenolate, which is a stronger electron donor, and thus enhances the ICT fluorescence emission (Fig. S8, ESI†).[12] Increased emission produces a higher on/off ratio, helping increase detection efficiency. In this study we used an organic base, tetrabutylammonium hydroxide (TBAH), to produce the basic reaction conditions (Fig. S5, ESI†), under which C6NIB was proven to be stable, i.e., no detectable change was observed in the fluorescence spectra within the experimental time (Fig. S2, ESI†). The fluorescence turn-on reaction of C6NIB was found to be dependent on the concentration of TBAH (Fig. S3, ESI†). When dispersed into silica gel, the optimal molar ratio of TBAH to C6NIB was determined to be 10:1. At the same molar ratio, the sensor composite of C6NIB–TBAH was comparatively investigated by dispersing it into three different supporting matrices, a silica gel thin layer chromatography (TLC) plate, an alumina TLC plate and a filter paper, and tested under the same vapor conditions of H_2O_2. Among the three matrices, silica gel exhibited a faster sensor response and the highest turn-on efficiency (Fig. S4, ESI†). Therefore, the sensor composite of C6NIB–TBAH dispersed in a silica gel TLC plate was used as the optimal sensor system in this study for vapor detection of H_2O_2.

TBAH is a highly hygroscopic liquid (similar to glycerol), and miscible with water and alcohols. A mixture of TBAH and C6NIB ethanol solutions is suited for dispersion into the silica gels. Vaporization of ethanol results in a homogeneous dispersion of C6NIB within the silica matrix. Such molecular dispersion is evidenced by the comparative absorption and fluorescence spectral measurements shown in Fig. 2, Fig. S7 and S8 (ESI†), which showed no significant difference in either absorption or fluorescence maxima between the ethanol solution and silica gel supported samples. The silica gel based sensor composite thus fabricated is expected to be efficient for vapor sampling of H_2O_2, which always coexists with water. The strong hygroscopy of TBAH, in combination with the large interface and porosity of silica gel, is highly conducive to vapor capture of water, as well as H_2O_2.

To examine the response speed of the sensor system, we measured the fluorescence spectral change of the C6NIB–TBAH composite dispersed in a silica gel TLC plate upon exposure to 1 ppm H_2O_2 vapor for varying time intervals (Fig. S6a, ESI†). The fluorescence emission centered at 553 nm increases gradually with exposure time, characteristic of the H_2O_2-mediated conversion of C6NIB to C6NIO. Since C6NIB has no measurable fluorescence emission in the long wavelength region, the reaction kinetics of the sensor can be simply monitored by measuring the emission intensity increasing with time (Fig. S6b, ESI†). The threshold of detectable emission can be set at an intensity level three times the standard deviation ($\sigma = 96$) of the emission intensity measurement; this corresponds to a sensor response time of ca. 0.86 s (as obtained from the fitted data in Fig. S6b, ESI†). This rapid sensor response towards H_2O_2 vapor is critical for real-time in-field detection of peroxides. To the best of our knowledge, there have been no fluorescent sensors reported that demonstrate such fast response to H_2O_2 vapor (particularly at a low level of 1 ppm). Indeed, expedient vapor detection of
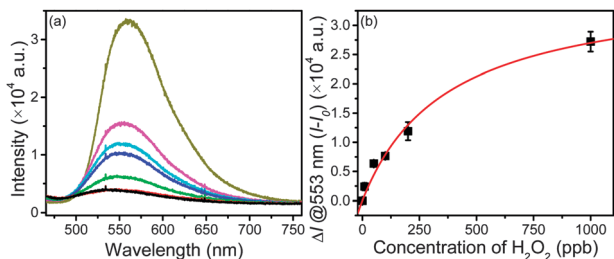
Fig. 3 (a) The fluorescence spectra of C6NIB dispersed in a silica gel TLC plate (the same as in Fig. 1d) measured before (base line) and after 5 min of exposure to various vapor concentrations of H_2O_2, 0 (pure water vapor, overlapped with the base line), 10, 50, 100, 200, and 1000 ppb. (b) A plot showing the emission intensity increase ΔI as a function of the vapor concentration of H_2O_2, for which the data points are fitted following the Langmuir adsorption model (see ESI†).

H_2O_2 demands combined materials optimization of sensors to afford efficient vapor sampling, strong interface binding and fast chemical reactions.

Taking advantage of the close to zero fluorescent background of C6NIB in the pristine state, the optimal sensor composite of C6NIB–TBAH dispersed in silica gel was expected to reach an unprecedented detection limit of H_2O_2 vapor by carefully measuring the turned on fluorescence intensity. To determine the detection limit, the silica gel TLC plate based sensor was exposed for 5 min to the vapor of aqueous solution of H_2O_2 in varying concentrations,[13] and the full fluorescence spectrum was recorded each time after the vapor exposure (Fig. 3). For a given exposure time, the fluorescence intensity increases with the vapor pressure (concentration) of H_2O_2. Fig. 3b shows the increase in fluorescence intensity measured at a maximal wavelength of 553 nm (relative to the value measured under pure water vapor) as a function of the vapor pressure of H_2O_2. Assuming that a quasi-equilibrium was reached within 5 min of exposure (as implied from the result shown in Fig. S6, ESI†), the results shown Fig. 3b should follow the Langmuir adsorption model (see ESI†). Indeed, the experimental data can be fit nicely into the Langmuir equation, with which we can project the detection limit. If defining an intensity increase as three times the standard deviation as the detectable signal, the detection limit for the current sensor material was projected to be 2.9 ppb, which corresponds to the vapor pressure of a H_2O_2 solution ca. 30 000 times diluted from the commercial 35 wt% solution. Such detection sensitivity is about two orders of magnitude better than that of the commercial fluorescence detector. It should be noted that the emission measurement employed in this study was based on an open sample holder, which was connected to the photon detector through an optical fiber. Such a simple measurement system usually suffers from a high noise level when measuring low intensity of emission, mainly due to the influence of scattered light and the significant light transport loss. We believe that upon integration into an enclosed optical detector, where the emission is directly measured by a photodetector aligned at right angle to the sensor, the same sensor material presented in Fig. 3 will be able to detect H_2O_2 vapor down to the level of sub ppb, simply by decreasing the signal-to-noise ratio by two to three orders of magnitude as previously practiced by Swager et al. with the Fido detector system.[14]

In summary, we have developed an expedient fluorescence turn-on sensor system that is suited for trace vapor detection of H_2O_2. The sensor mechanism is based on H_2O_2-mediated oxidation of a boronate fluorophore, C6NIB, which is non-fluorescent in the ICT band, but turns out to be strongly fluorescent upon conversion into the phenol state, C6NIO. This fluorescence turn-on reaction is extremely selective towards H_2O_2, with no sensor response to other common reagents. The negligible fluorescence background of C6NIB, combined with the high fluorescent emission of C6NIO, makes C6NIB an ideal candidate for efficient sensing. Dispersing C6NIB with TBAH into a silica gel matrix produces a highly efficient sensor system for vapor detection of H_2O_2, in terms of both detection limit (down to 2.9 ppb) and response time (down to 1 s under 1 ppm H_2O_2).

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