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. For vapor detection, fluorescent sensing represents a simple, rapid, and highly sensitive technology. Recently, fluorescence “turn-on” (or enhancement) molecular sensors have drawn increasing attention for explosive detection, 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. Hydrogen peroxide ($\text{H}_2\text{O}_2$) is usually considered as a signature compound for detecting peroxide explosives, from which $\text{H}_2\text{O}_2$ 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 $\text{H}_2\text{O}_2$ becomes critical for these security scenarios.

Although various methods and technologies have been developed to detect $\text{H}_2\text{O}_2$, such as the electrochemical method, colorimetric and fluorimetric method, vapor detection of $\text{H}_2\text{O}_2$ (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 $\text{H}_2\text{O}_2$ (for efficient vapor sampling), but also an expedient, selective reaction with $\text{H}_2\text{O}_2$ to transduce the readable signal. While a few recent papers reported on fluorescence turn-on sensors that can be employed for vapor detection of $\text{H}_2\text{O}_2$, 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 $\text{H}_2\text{O}_2$ 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, we report herein on a new fluorescence turn-on sensor for $\text{H}_2\text{O}_2$, 2-hexyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-benzo-[de]isoquinoline-1,3(2H)-dione (C6NIB). This molecule is only weakly fluorescent in the UV region ($\lambda_{\text{max}}$ 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 $\text{H}_2\text{O}_2$ the ary1 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-1H-benzo[de]isoquinoline-1,3(2H)-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. Before the addition of $\text{H}_2\text{O}_2$, the ethanol solution of C6NIB exhibited no detectable emission in the ICT band, whereas strong emission was observed in the presence of $\text{H}_2\text{O}_2$ (Fig. 2b). Such a fluorescence turn-on reaction is intrinsically selective for $\text{H}_2\text{O}_2$, 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 $\text{H}_2\text{O}_2$, which has been proven by previous studies in solutions, whereas the boronate molecules are based on different backbone structures.
The high chemical selectivity, together with the high fluorescence turn-on sensitivity, makes C6NIB an ideal sensor for vapor detection of H$_2$O$_2$, 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$_2$O$_2$ 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. 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. Nonetheless, once the molecule is modified with an electron deficient group like boronate, it will become a strong electrophile with increasing reactivity with H$_2$O$_2$. The H$_2$O$_2$-mediated oxidation of aryI boronates is kinetically favored under basic conditions, which facilitates the dissociation of H$_2$O$_2$ into the HO$_2^-$ anion (acting as a nucleophile) that can in turn react with the boronate group (a strong electrophile). 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†). 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$_2$O$_2$. 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$_2$O$_2$.

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 and 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$_2$O$_2$, 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$_2$O$_2$.

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$_2$O$_2$ vapor for varying time intervals (Fig. S6a, ESI†). The fluorescence emission centered at 553 nm increases gradually with exposure time, characteristic of the H$_2$O$_2$-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 fluorescence emission time of ca. 0.86 s (as obtained from the fitted data in Fig. S6b, ESI†). This rapid sensor response towards H$_2$O$_2$ 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$_2$O$_2$ vapor (particularly at a low level of 1 ppm). Indeed, expedient vapor detection of
H₂O₂ 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 a silica gel was expected to reach an unprecedented detection limit of H₂O₂ 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 H₂O₂ in varying concentrations, 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 H₂O₂. 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 data points are fitted following the Langmuir adsorption model (see ESI†).

Notes and references


