

# A Novel Optical Ozone Sensor Based on Purely Organic Phosphor

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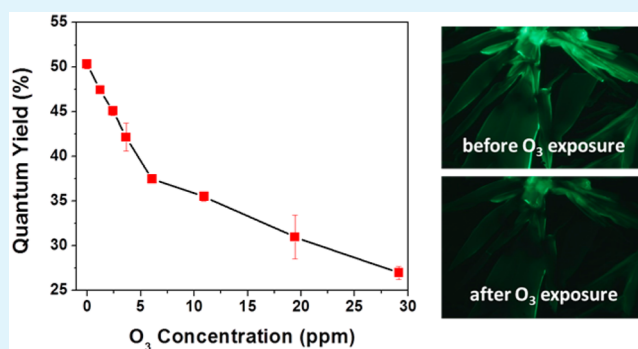
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## S Supporting Information

**ABSTRACT:** An optical ozone sensor was developed based on the finding that a purely organic phosphor linearly loses its phosphorescence emission intensity in the presence of varying concentration of ozone gas and ozonated water. Compared to conventional conductance-based inorganic sensors, our novel sensory film has many advantages such as easy fabrication, low-cost, and portability. NMR data confirmed that phosphorescence drop is attributed to oxidation of the core triplet generating aldehyde group of the phosphor. We observed that linear correlation between phosphorescence and ozone concentration and it can detect ozone concentrations of 0.1 ppm that is the threshold concentration harmful to human tissue and respiratory organs. Like a litmus paper, this ozone sensor can be fabricated as a free-standing and disposable film.

**KEYWORDS:** optical ozone sensor, organic phosphorescence, aldehyde oxidation



Ozone sensing has recently attracted great interest because ozone, which is hazardous to humans, is produced by many industrial uses such as surface cleaning of semiconductor devices and biomaterials.<sup>1,2</sup> As an environmentally clean oxidant or disinfectant, ozone is also used in water sterilization and deodorization of drinking water.<sup>3</sup> Furthermore, ozone is generated indoor by office machinery such as photocopiers and laser printers. However, long-time exposure to ozone at high concentration can cause health problems like pulmonary edema, so it is of great importance to detect accurate environmental ozone concentration.<sup>4</sup> Ozone has been widely sensed by monitoring conductance changes in metal oxide-based inorganic semiconductor devices that feature high sensitivity, low cost, and simple fabrication.<sup>5,6</sup> Among metal oxides, zinc oxide (ZnO) received more attention as a gas sensor because of its high sensitivity, nontoxicity, and high chemical stability.<sup>7</sup> To further enhance sensitivity of ZnO-based ozone sensors, researchers have developed nanostructure fabrication.<sup>8,9</sup>

Ozone is by nature a highly unstable and reactive oxidizing species with much higher oxidation power than that of oxygen. It is difficult to reversibly reduce the oxidized surface of metal oxides, which limits reversible sensing.<sup>10</sup> Therefore, the conventional semiconductor-based sensors require high temperature operation, above 200 °C, so as to reduce the oxidized surface for reversible sensing.<sup>11</sup> These conventional metal oxide-based sensors with an integrated heating system are not suitable for low-cost fabrication because of high operating temperatures and high power consumption of the heating system. Alternately, these metal oxides can be reduced by UV

light and reoxidized by ozone exposure, which enables reversible sensing at room temperature.<sup>12</sup> In this case, the conventional thermal reactivation process of the sensing layer is substituted with external UV irradiation. This photoassisted reversible oxidation and reduction mechanism has been further investigated.<sup>13,14</sup> Bender et al. showed that a ZnO ozone sensor was photoreduced by UV light exposure in vacuum and the conductivity was recovered accordingly.<sup>13</sup> Wang et al. used a 400 nm light-emitting diode to reduce the oxidized surface of In<sub>2</sub>O<sub>3</sub> ozone sensor.<sup>14</sup>

Optical ozone detection has been garnering interests because optical detection is free from electromagnetic noise and compatible with optical fibers for remote sensing.<sup>15,16</sup> Several optical ozone detection methods have been reported including UV absorption photometry,<sup>17</sup> IR absorption photometry,<sup>18</sup> chemiluminescence,<sup>19</sup> and photoluminescence (fluorescence).<sup>20,21</sup> UV or IR absorption methods are not suitable for compact and low cost devices, in spite of their relatively accurate and reliable operation. Chemiluminescence and photoluminescence are highly sensitive, but these methods commonly lack reversibility. Amos reported ozone sensing by means of 2-diphenylacetyl-1,3-indandione-1-hydrazone as a fluorophor, but the sensor suffered from rather slow response and mediocre sensitivity.<sup>20</sup> Guoquan et al. utilized fluorescence quenching to detect atmospheric ozone using 2',7'-dichloro-

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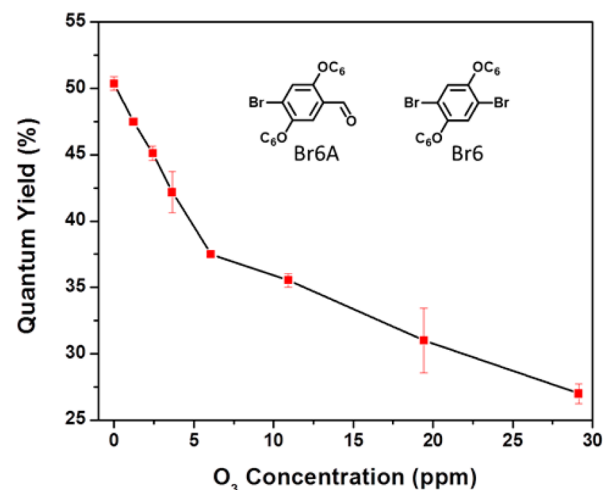
fluorescein, which however required precise pH control.<sup>21</sup> Moreover, fluorescence-based photometry must be conducted in solution, which is incompatible with a desirable portable and facile sensory platform. Therefore, small-size portable ozone sensors, especially those can be integrated with any kind of mobile devices, are of great interest.

In this contribution, we present our recent development of a rapid, sensitive, cost-effective, and portable sensory system based on organic phosphorescence to detect ozone gas and ozonated water. We synthesized a purely organic phosphor (Br6A) using a previously reported method.<sup>22</sup> In a doped crystal with its analogous host material (Br6), Br6A shows bright green phosphorescence emission with high photoluminescent quantum efficiency. However, it is easily oxidized by ozone exposure resulting in a decreased phosphorescence quantum yield (QY). This phosphorescence drop is induced by oxidation of aldehyde, its triplet generating core moiety. To obtain a free-standing sensory film, we blended the phosphor (Br6A) with an amorphous glassy polymer, isotactic poly(methyl methacrylate) (iPMMA).<sup>23</sup> The resulting blend film showed a predictable and quantifiable quantum efficiency change with increased ozone exposure time in the same fashion as the doped Br6A crystal did. The free-standing film is applicable to monitor ozone concentration in the form of gas or solution. To the best of our knowledge, this unique ozone sensor is the first solid-state sensor with signal transduction via organic phosphorescence change. As a free-standing, disposable, and colorimetric sensory film like a litmus paper, this would be one of the most convenient platforms as a portable ozone sensor, and the cost effectiveness can compensate for the limited reversibility.

As a purely organic phosphor, Br6A is weakly emissive under ambient conditions because of the dominant vibrational loss pathway even though it contains a good triplet generating moiety, the aromatic ketone. However, it emits bright room-temperature phosphorescence once it is intermixed with an analogous dibromo compound (Br6), which has a good crystalline character and forms a well-defined doped crystal.<sup>22</sup> In the doped crystal, vibration is efficiently suppressed by halogen bonding and intersystem crossing is also facilitated by heavy atom effect induced by the halogen bonding. These effects make the doped crystal relatively robust under ambient atmosphere, unlike other purely organic alternatives. Br6A is also quite emissive at room temperature if it is embedded into a glassy polymer matrix like isotactic PMMA.<sup>23</sup> In this composite, vibration is suppressed by rigidity of the matrix polymer, and intersystem crossing is enhanced at a certain mixing concentration through intermolecular halogen bonding.<sup>23,24</sup> This amorphous phosphorescence system has a number of advantages over crystal-based phosphorescence, such as, easy free-standing film formation and no need for stringent crystal growth. Its phosphorescence emission also shows good stability in ambient conditions partly because of the rigidity of polymer, limited oxygen permeability through the polymer matrix, and suppression of the associated phosphorescence quenching pathways.

Interestingly, these two phosphorescence systems are quite sensitive to ozone, a highly active species, and show a predictable emission efficiency drop by varying ozone concentration. First, we prepared doped crystals consisting of 10 wt % of Br6A versus Br6 to detect ozonated water with different ozone concentration. This crystalline sample has a 50.4% initial QY at room temperature. After submerging the

sample in deionized water, ozone was generated and adsorbed into the water. The resulting sample was rinsed with deionized water and dried at room temperature, followed by QY measurement. Ozone concentration was determined by a titration method with a  $\text{Na}_2\text{S}_2\text{O}_3$  solution using ozonated water containing KI and starch.<sup>25</sup> As shown in Figure 1, QY tends to



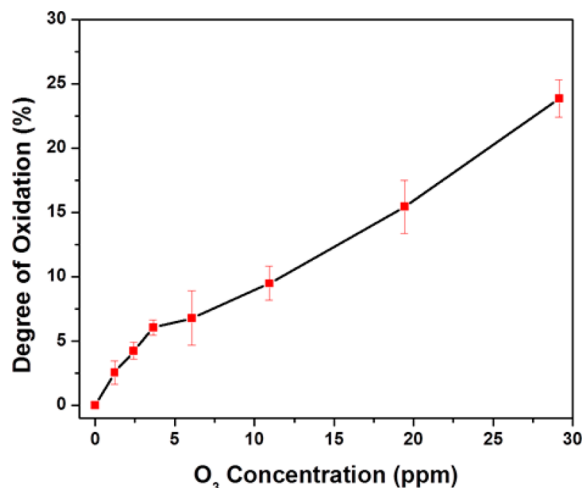
**Figure 1.** Phosphorescence QY change of doped crystal as a function of ozone concentration. Chemical structures of Br6 and Br6A are shown. The excitation wavelength was 365 nm, and the phosphorescence emission was collected in the range of 450–620 nm.

decrease as a function of ozone concentration. QY decreased more rapidly, with a rate of 4.21% per 1 ppm of ozone, at low concentration (below 6 ppm) than at high concentration (0.90% QY decrease per 1 ppm of ozone above 6 ppm). We believe that at the early stage of ozone exposure, most of the adsorbed ozone can easily react with the crystal film surface, leading to fast QY drop. However, at the later stage with higher ozone concentration, slow penetration of the adsorbed ozone through the crystal structure combined with the fact that water is a poor solvent for the crystal result in the slower QY drop. As one can clearly see, the QY drop up to the ozone concentration of 6.07 ppm shows a very good linear correlation implying possible quantitative detection of ozone concentrations of 0.1 ppm that is the threshold concentration that damages human tissue and respiratory organs.

It has been well-known that aldehyde is easily oxidized to carboxylic acid or peroxy acid by ozone.<sup>26</sup> Ozonation mechanism is explained by two competitive pathways. The first one is acyl hydrogen abstraction followed by forming a hydrotrioxide as an intermediate, finally converted to carboxylic acid.<sup>27</sup> The other is stepwise cycloaddition leading to a tetroxolane intermediate followed by ring opening of the tetroxolane, finally producing carbonyl oxide.<sup>28</sup> Based on the knowledge from those references, we hypothesized that aldehyde, a critical triplet producing moiety, was oxidized by ozone, resulting in consequential phosphorescence quenching. In order to investigate aldehyde oxidation with ozone, we collected NMR spectra of each sample as shown in Figure S1 in the Supporting Information. Aldehyde and aromatic hydrogen peaks appear at 10.40, 7.29, and 7.21 ppm, respectively. Notably, the aldehyde proton peak area decreased relative to that of the aromatic hydrogen. To analyze quantitatively, each peak was integrated and normalized by the aldehyde hydrogen area. The degree of oxidation was defined as

$$(1 - I_{\text{air}}/I_{\text{ozone}})100 \quad (1)$$

where  $I_{\text{air}}$  and  $I_{\text{ozone}}$  represent relative peak area of the aromatic hydrogen to the aldehyde under air and ozone atmosphere at a given concentration, respectively. Our data clearly show that the degree of oxidation tends to increase with ozone concentration, as shown in Figure 2. This increase in oxidation



**Figure 2.** Degree of oxidation of the aldehyde moiety in Br6A as a function of ozone concentration based on areal integration of NMR data. Aldehyde and aromatic hydrogen peaks appear at 10.40, 7.29, and 7.21 ppm, respectively.

with ozone concentration is closely related to the QY decrease as shown in Figure 1. Compared to the later stage above 6 ppm ozone, the aldehyde is more rapidly oxidized at the early stage below 6 ppm, which is likely attributed to the different accessibility of adsorbed ozone to the surface and the inside of the crystal.

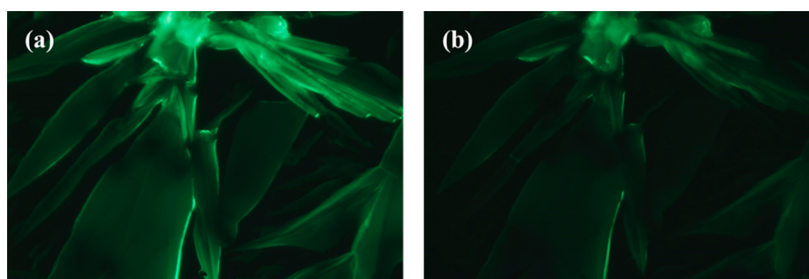
To investigate morphological change by ozone exposure, we collected fluorescence microscope images as shown in Figure 3. The green phosphorescence intensity clearly decreased after the doped crystals were submerged in 6.07 ppm ozonated water, whereas there was no significant change in morphology. This finding implies that QY drop is solely attributed to chemical oxidation of aldehyde, not by physical appearance change.

To further investigate the oxidation of the aldehyde moiety, we prepared slowly grown Br6A pure crystal having phosphorescence QY of 2.9%. Interestingly, we found that Br6A itself was not oxidized even after being treated for 30 min in ozonated water without any phosphorescence change, which was supported by NMR data in Figure S2 in the Supporting Information. We hypothesized that Br6 in the doped crystal

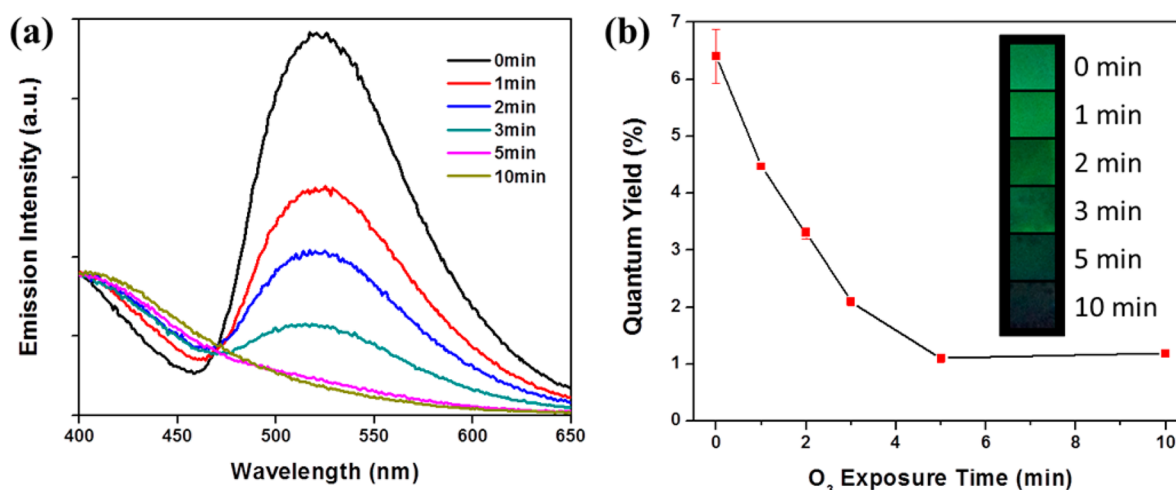
plays a key role in the aldehyde oxidation. It has been reported that catalytic oxidation of aldehydes can be promoted by Lewis acids.<sup>29,30</sup> In our system, by acting as a Lewis acid Br6 promotes the oxidation of the Lewis basic, aldehyde functional group of Br6A. Thus, we concluded that proximity between Br6 and Br6A by intermolecular halogen bonding facilitates Lewis acid-catalyzed ozonation of Br6A.

Even though the crystal-based optical ozone sensor has many advantages, such as rapid response time and high sensitivity, it must be fabricated by dropcasting or spin-coating onto a substrate. As a free-standing sensor without any substrate, an amorphous phase optical sensor consisting of a phosphor as a sensory unit embedded in a polymer matrix was developed. Here, PMMA does not only act as a rigid matrix to suppress triplet vibration of Br6A, but it also provides a good processability to form free-standing phosphorescence films sensitive to ozone. This feature enables the fabrication of a portable and low cost sensor like a litmus paper. A 1 wt % of chloroform solution containing 5 wt % of Br6A of the polymer mass was prepared and dropcast on a silicon wafer substrate and dried at room temperature followed by thermal annealing at 100 °C for 10 min. The resulting film was easily peeled off from the substrate and showed 6.5% green phosphorescence QY under ambient conditions. It was exposed directly to ozone gas generated by UV-ozone procleaner. As shown in Figure 4a, green phosphorescence emission intensity decreases with increasing ozone exposure time and it loses most of its phosphorescence after exposure for 5 min. Data clearly show a linear correlation between QY and ozone exposure time from the initial state to 3 min ozone exposure. From the proton NMR spectra in Figure S3 in the Supporting Information, we found that most of the aldehyde peak disappeared after 5 min of ozone exposure.

In summary, we developed an optical ozone sensor based on a purely organic phosphor showing high sensitivity and linear correlation between QY and ozone concentration. The observed phosphorescence QY drop is due to oxidation of the aldehyde moiety of the organic phosphor that is the main triplet generating functional group of Br6A. It can quantitatively detect both ozone gas and ozonated water. The sensitivity of the system can detect ozone concentrations of 0.1 ppm, which is the threshold concentration harmful to human tissue and respiratory organs. This novel sensor has a number of benefits over conventional conductance-based inorganic sensors including portability, easy fabrication, and low cost. Like a litmus paper, this ozone sensor can be fabricated as a free-standing and disposable film. The development of this sensor technology should enable facile ozone detection, which will help improve the quality of life and safety for workers in ozone producing industries. The low cost of this sensor is suitable for broad



**Figure 3.** Fluorescence microscope images of (a) pristine-doped crystal and (b) ozone-treated doped crystal in 6.07 ppm ozonated water.



**Figure 4.** (a) Phosphorescence emission intensity change and (b) QY change of amorphous ozone sensor as a function of ozone concentration (inset: fluorescence microscope images were taken under 365 nm light). The excitation wavelength was 365 nm, and phosphorescence emission was collected in the range of 450 to 620 nm.

adaptation as a means of identifying malfunctioning of ozone producing equipment and indicating overexposure to this harmful chemical.

## ■ ASSOCIATED CONTENT

### Supporting Information

Proton NMR, experimental details including materials, measurement, and ozone sensing. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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