

# Conjugated Polymer–Titania Nanoparticle Hybrid Films: Random Lasing Action and Ultrasensitive Detection of Explosive Vapors

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We have first demonstrated that a random laser action generated by a hybrid film composed of a semiconducting organic polymer (SOP) and TiO<sub>2</sub> nanoparticles can be used to detect 2,4,6-trinitrotoluene (TNT) vapors. The hybrid film was fabricated by spin-casting SOP solution dispersed with nanosized TiO<sub>2</sub> particles on quartz glass. The SOP in the hybrid film functioned as both the gain medium and the sensory transducer. A random lasing action was observed with a certain pump power when the size (diameter of 50 nm) and concentration ( $8.9 \times 10^{12}/\text{cm}^3$ ) of TiO<sub>2</sub> nanoparticles were optimized. Measurements of fluorescence quenching behavior of the hybrid film in TNT vapor atmosphere (10 ppb) showed that attenuated lasing in optically pumped hybrid film displayed a sensitivity to vapors of explosives more than 20 times higher than was observed from spontaneous emission. This phenomenon has been explained with the four-level laser model. Since the sensory transducer used in the hybrid polymer/nanoparticles system could be replaced by other functional materials, the concept developed could be extended to more general domains of chemical or environment detection.

## 1. Introduction

A growing emphasis has been devoted to finding new materials and device architectures to enhance the sensitivity of sensors for chemical and biological agents of security concern.<sup>1–4</sup> Among the new sensory materials that have been developed, semiconducting organic polymers (SOPs) are of particular interest because of the amplified detection arising from the facile excited state (exciton) transport.<sup>5–9</sup> The success in detection of ultratrace explosives, such as 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT), using SOP-based photoluminescence sensors have been reported,<sup>3</sup> and the detection mechanism has been defined as an electron-transfer quenching of fluorescence from electron-deficient nitroaromatics.<sup>2</sup> The low vapor pressure of DNT and TNT (about 100 and 5 ppb, respectively) and their efficiency for reversible fluorescence quenching make them ideal analytes to explore novel sensitivity enhancement mechanisms in SOP sensors.<sup>5</sup>

Recently, a new sensitivity enhancement mechanism has been developed by Swager et al. who demonstrated how a lasing action in organic polymers can be used to improve the sensitivity to nitroaromatic explosives.<sup>5</sup> They found that amplified spontaneous emission (ASE) signal was up to 30 times more sensitive to quenching compared to the spontaneous emission upon exposure of a SOP film to saturated DNT vapor for 1 s. By using a distributed feedback (DFB) grating structure, they achieved higher sensitivity to saturated TNT vapor. However, the high cost and relatively complex fabrication of the ultraviolet band DBF gratings restrict its applications.

The systems with strong scattering and gain have been attracting growing attention, particularly following the observa-

tion of lasing action in dye solution,<sup>10</sup> semiconductor powder,<sup>11</sup> human tissues,<sup>12</sup> and dye-infiltrated photonic glass.<sup>13</sup> The multiple light scattering in these systems replaces the standard optical cavity of traditional lasers and the interplay between gain and scattering determines the lasing properties.<sup>14</sup> Unlike in ordinary lasers, the resulting light emission is multidirectional; thus such a laser is called a “random laser”.<sup>15–17</sup> A major advantage of random lasers over regular lasers is their easy preparation and low cost. However, such lasers based on SOPs have rarely been investigated.

In this paper, we report an ultrasensitive explosive sensor based on a low-cost hybrid film composed of a conjugated polymer, poly(triphenylamine-*alt*-phenylene vinylene) (TPA-PPV), and TiO<sub>2</sub> nanoparticles. We have found that the multiple light scattering from nanosized TiO<sub>2</sub> can impart the hybrid film with a random lasing action. Although random lasing has been reported by other groups in various random systems,<sup>14</sup> the major difference of our material system is that SOP functions as both the gain medium<sup>18–21</sup> and sensor transducer element. To our knowledge, this is the first to demonstrate the use of random lasing action generated from a hybrid SOP film containing TiO<sub>2</sub> nanoparticles to detect explosive vapors with conversably enhanced sensitivity.

## 2. Experimental Section

**2.1. Reagents and Instruments.** Poly(triphenylamine-*alt*-phenylene vinylene) (TPA-PPV) was synthesized via HORNER reaction between 4,4'-diformyl triphenylamine and 1,4-xylylene-bis(dimethylphosphate). TiO<sub>2</sub> was bought from Shanghai Shanghui Nano Ltd. Polystyrene (PS), trimethylchlorosilane (TMCS), and triethylamine (TEA) were purchased from Sinopharm Chemical Reagent Co., Ltd. All other chemicals were of analytical grade. UV-vis absorption and fluorescence spectra of TPA-PPV were measured with a JASCO V-670 spectrophotometer and a JASCO FP-6500 spectrometer, respectively. The fluorescence spectra were measured using excitation band width

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3 nm and emission band width 1 nm. Scanning electron microscope (SEM) measurements were performed with a Hitachi S4700. The as-prepared sensor film was optically pumped by frequency-tripled output of a Nd:YAG laser (355 nm, 10 Hz repetition rate, 5 ns pulse width) (Quanta-Ray INDI 40, Spectra-Physics). The laser energy was detected by 818E Energy Detector (Newport) and recorded by 1918-c Optical Meter (Newport). The emission was collected by an optical fiber bundle linked with an ICCD spectrometer (Shamrock SR-500, ANDOR Technology). For measuring the sensor property, a sensor film was inserted into a sealed glass cuvette (20 mL size) at room temperature containing TNT and cotton, which prevents direct film analyte contact and helps to maintain a constant TNT-saturated vapors.

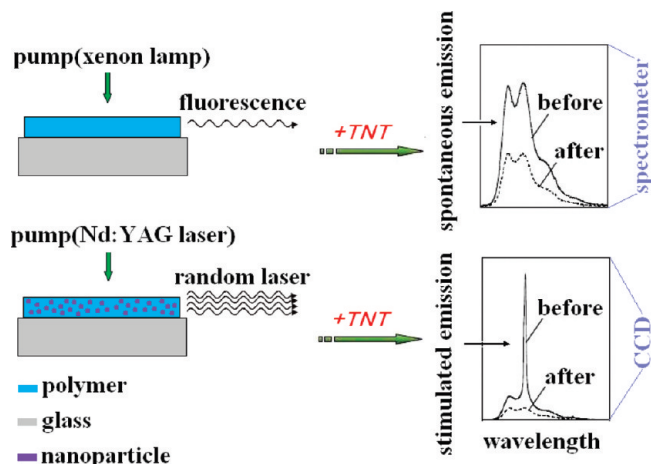
**2.2. Surface Modification of TiO<sub>2</sub> Nanoparticles.** Our initial attempts to produce hybrid films of TPA-PPV:TiO<sub>2</sub> were hampered by aggregation of hydroxyl-terminated TiO<sub>2</sub> particles. Thus, we modified the polar surface of TiO<sub>2</sub> nanoparticles. Trimethylsilylation (TMS) functionalized nanosized TiO<sub>2</sub> was synthesized according to literature.<sup>22</sup> The reaction was conducted on the basis of the Schlenk technique. To a suspension of 150 mg of TiO<sub>2</sub> in 10 mL of methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>) was added 5 mL of TEA, followed by the addition of 5 mL of TMCS. The reaction was kept at room temperature in an inert atmosphere for 24 h. Then the reaction mixture was quenched with deionized water, filtered through 0.45  $\mu$ m filter membrane, and washed with deionized water thoroughly. Surface-modified TiO<sub>2</sub> was dried under vacuum and ready for SEM measurements.

**2.3. Preparation of Polymer–TiO<sub>2</sub> Nanoparticles Hybrid Films.** The hybrid film was fabricated by spin-casting a solution of TPA-PPV and PS containing well-dispersed TiO<sub>2</sub> nanoparticles on quartz plates. The different quantities of PS were added to the TPA-PPV solutions (typically  $1.26 \times 10^{-2}$  M in tetrahydrofuran) to improve the film-forming ability and fluorescence quantum yield.<sup>22</sup> The desired amount of TiO<sub>2</sub> was added to the polymer solutions and dispersed by additional stirring to form concentration of  $8.9 \times 10^{12}/\text{cm}^3$ .<sup>23</sup> Disordered hybrid films with various PS content were then prepared by spin-casting the hybrid solutions with a speed of 1500 rpm (round per minute) on quartz substrates. The prepared films were then dried overnight in a 50 °C vacuum oven for subsequent measurements.

**2.4. Measurements of Photoluminescence and Sensing Characteristic.** The measurement system used to characterize the performance of sensor device using lasing technique was schematically shown in Figure 1 (bottom). The sensor film was optically pumped by frequency-tripled output of a Nd:YAG laser with the pump beam perpendicularly focused to a 1 mm spot. The emission was collected from the edge and surface by an optical fiber bundle linked with an ICCD spectrometer. The real-time photoluminescence spectra of the film were recorded in the spectrometer by changing the pump laser energy. Simultaneously, the photostability data of the films could be obtained by fixing the laser energy in a certain time. For sensory measurements, the film was quickly inserted into a glass cuvette filled with TNT-saturated vapors using the same experimental configuration as above. The real-time attenuated lasing intensity was recorded for the next sensitivity characterizations.

### 3. Results and Discussion

The two ingredients that are crucial for a random laser are optical gain amplification and a disordered material that provides multiple scattering of light. The SOP materials used in our hybrid film sensor, TPA-PPV, emit green light at wavelength  $\lambda$

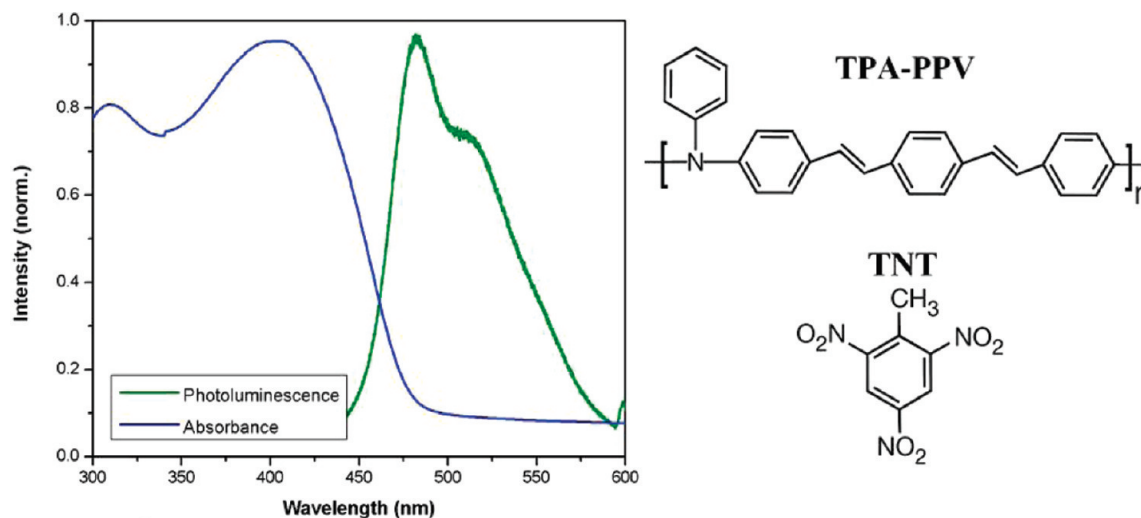


**Figure 1.** Schematic of the measurement systems used to characterize the performance of sensor device using conventional fluorescence (top) and new lasing (bottom) techniques.

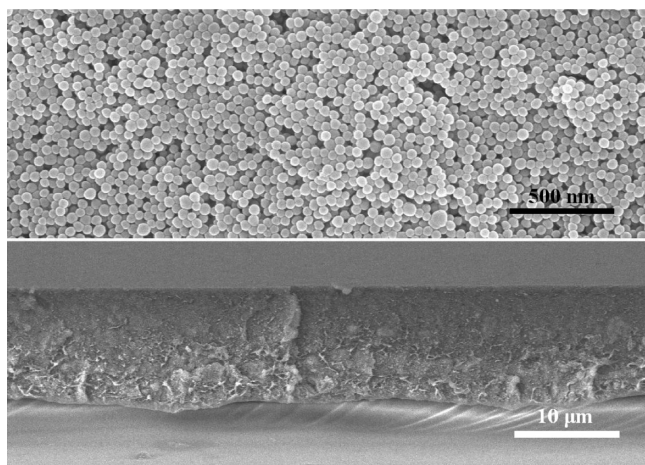
= 481 nm (with shoulder  $\lambda = 510$  nm) (Figure 2) and also exhibit sensitivity to the chosen analyte, TNT. Its fluorescence quantum yield in benzene can be almost up to 1.00 relative to perylene ( $\Phi = 0.94$ ).<sup>24</sup> The introduction of triphenylamine (TPA) on polymer chains interrupts the  $\pi$ - $\pi$  conjugation system of the phenylene vinylene (PPV) backbone, which prevents the excitons from migrating to traps and consequently the ratio of nonradiative process is reduced.<sup>24</sup> On the other hand, the additional  $\pi$ -electron delocalization between the nonpaired electron in the nitrogen atom and  $\pi$ -electrons in the conjugated units contributes to the improvement of its photoluminescence efficiency,<sup>24</sup> which facilitates lasing action in the hybrid films.<sup>22</sup>

Our initial attempts to produce hybrid films of TPA-PPV:TiO<sub>2</sub> were hampered by aggregation of hydroxyl-terminated TiO<sub>2</sub> particles. After the surface modification, we found that the suspension composed of TiO<sub>2</sub> nanoparticles was stable for hours at room temperature. From Figure 3 (top), we could see that the agglomeration of TiO<sub>2</sub> nanoparticles in tetrahydrofuran decreased considerably. As a result, TPA-PPV:TiO<sub>2</sub> hybrid films could be fabricated easily. In our hybrid films, the benefit of using TiO<sub>2</sub> is that it has a large refractive index ( $n \approx 2.5$ ) compared to the polymer ( $n_p \approx 1.7$ ), which affords strong scattering for random lasing.<sup>10</sup> The selected size (diameter of 50 nm) and concentration ( $8.9 \times 10^{12}/\text{cm}^3$ ) of the TiO<sub>2</sub> nanoparticles facilitate the generation of the random laser, which is the resulting transport mean free path (the average distance over which the scattered light direction is randomized) in the hybrid film,  $l_t \ll L$ ,<sup>13,14</sup> where  $L$  is the sample size (Figure 3, bottom).

For photoluminescence measurements, the films were optically pumped by the frequency-tripled output of a Nd:YAG laser. Figure 4a shows the emission spectra of the as-prepared hybrid films under different pump intensities. At low excitation intensity, the spectrum consisted of a single broad spontaneous emission peak. With an increase in the pump power to a certain value, the width of the emission spectrum (fwhm, full width at half maximum) decreased rapidly to 5 nm. The threshold behavior ( $E_{th} = 191 \text{ mJ}/\text{cm}^2$ ) of random lasing could be clearly seen in Figure 3b. The peak at  $\lambda = 510$  nm is in accordance with the first vibronic transition (0, 1) wavelength of TPA-PPV. The (0, 0) transition, corresponding to the peak at  $\lambda = 480$  nm, dominates the spontaneous emission owing to its higher oscillator strength. The lasing action from the (0, 1) mode is probably governed by the reabsorption losses that inhibit lasing



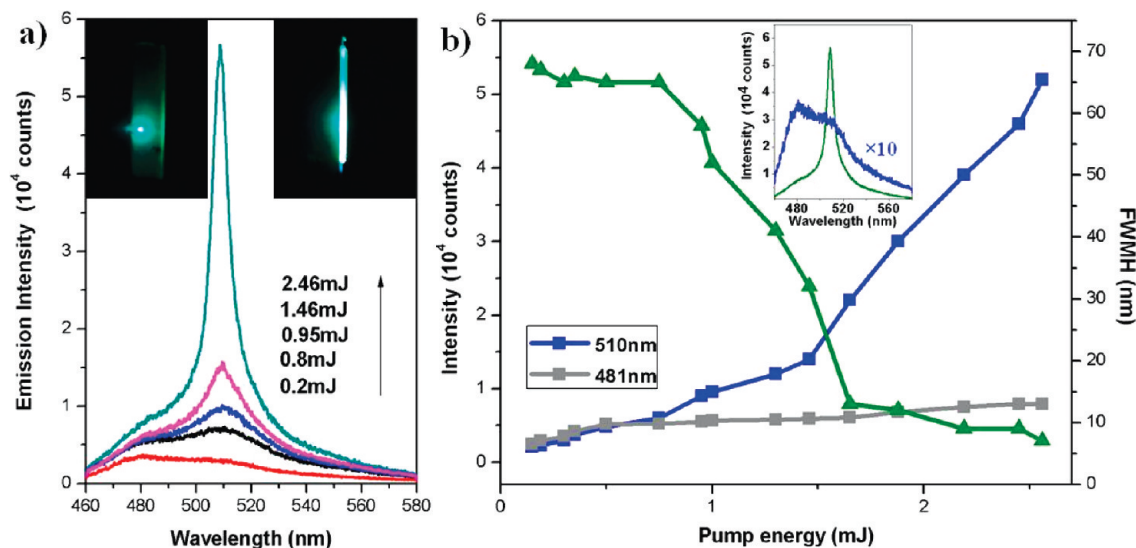
**Figure 2.** Normalized absorption and photoluminescence spectra of a spin-coated TPA-PPV film on a quartz plate (from a tetrahydrofuran solution, TPA-PPV concentration =  $2.43 \times 10^{-5}$  M). Right: chemical structure of polymer TPA-PPV and TNT.



**Figure 3.** Scanning electron microscope (SEM) images of the modified nanosized  $\text{TiO}_2$  by dip-coating a tetrahydrofuran suspension on quartz glass (top) and a hybrid film of TPA-PPV/PS with dispersed  $\text{TiO}_2$  nanoparticles on quartz plate by spin-casting process (bottom).

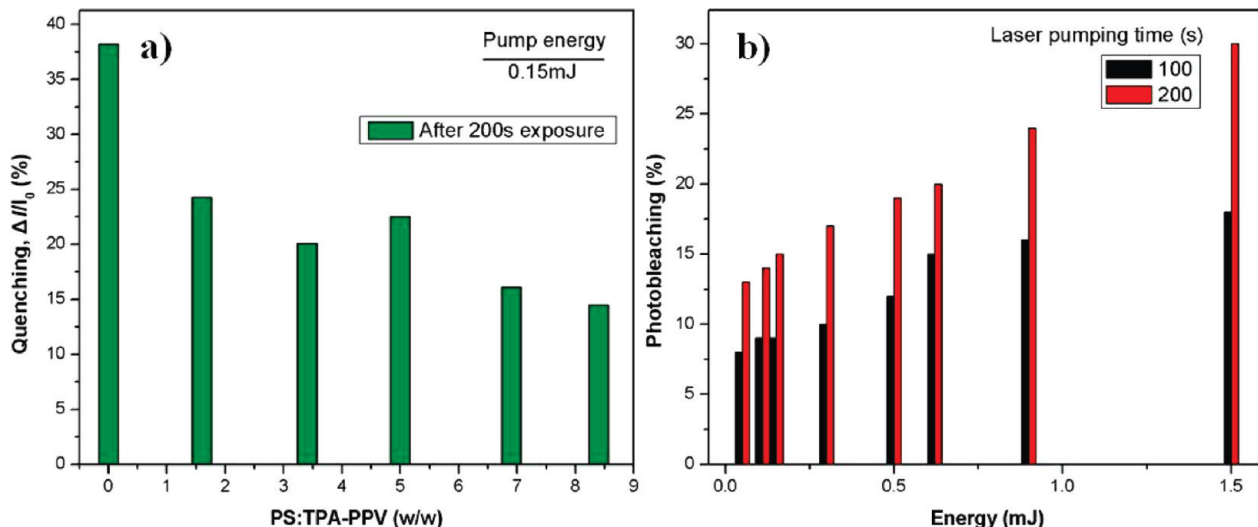
from the (0, 0) transitions. We have checked the multidirectional emission by collecting the emission in two other directions ( $60^\circ$  and  $15^\circ$  to the sample surface), and overall narrowing of spectrum was also observed, a typical characteristic of random laser (see Supporting Information, Figure S1).<sup>11,23</sup>

The influence of PS content and the photostability of the hybrid film was carefully studied. To avoid a large decline of sensory performance by introducing PS, the blend films with different PS/TPA-PPV ratios were prepared and the influence of the PS proportion on the film sensitivity was examined. Figure 5a reveals a gradually declined sensitivity with increasing the PS portion in the hybrid film for the sensory responses at lasing peak  $\lambda = 510$  nm in TNT vapor. When PS:TPA-PPV (w/w) was 3–4, there was a balance between the sensory performance and the lasing threshold. On this basis, an optimized PS:TPA-PPV ratio was determined. The photostability of the hybrid film was investigated by exposing it to laser light in air without TNT vapors. The photobleaching data at the lasing peak  $\lambda = 510$  nm, after 100 and 200 s of pumping were shown in Figure 5b.



**Figure 4.** (a) Emission spectra collected from the edge of a blend polymer film under uniform excitation, as a function of increasing pump energy at room temperature. Inset: pumping the film with a  $\lambda = 355$  nm pulse beam resulted in a multidirectional emission output, front view (left) and side view (right), with the pump energy above the threshold. (b) Plot of the lasing emission peak ( $\lambda = 510$  nm) intensity (blue squares), spontaneous emission peak ( $\lambda = 481$  nm) intensity (gray squares) and fwhm (olive triangles) versus pump energy for the film shown in (a). Inset: emission spectra excited with the light energy below (0.2 mJ, blue) and above threshold (2.4 mJ, olive) emission spectra.





**Figure 5.** (a) Sensory responses versus the proportion of PS in the hybrid film after 200 s exposure to TNT under the same excitation energy (0.15 mJ, lasing peaks  $\lambda = 510$  nm, pumping time 200 s). (b) Photobleaching data at the lasing peak  $\lambda = 510$  nm, after 100 and 200 s pumping with different energies in air.

To avoid the impact from the photobleaching, a short pumping time should be used. In the following experiments, 100 s of pumping time was chosen.

To validate the enhanced sensing principle driven by lasing action, we have made comparisons of the sensory responses of the spontaneous emission and lasing emission of the film sample to a static saturated vapor of TNT (10 ppb). The different sensitivity is readily apparent in the polymer film before and after a 100 s exposure to TNT (Figure 6a–c), wherein the spontaneous emission at  $\lambda = 481$  nm displays approximately 30% quenching independent of laser power. However, when the excitation levels ( $E = 2.2$  mJ) are above the threshold power, the  $\lambda = 510$  nm lasing emission displays a 29-fold drop in intensity (Figure 6d) and 1.8-fold rise in quenching efficiency (attenuation of intensity divided by initial intensity) (Figure 6d inset).

To further reduce the photobleaching, we shortened the response time to 10 s, in which photobleaching could be basically neglected. As shown in Figure 6e, a significant attenuation in the lasing peak, which is 20-fold sensitive than that in the spontaneous peak, was obtained, implying 4-folds of enhancement in sensitivity.

The conventional sensory devices for explosive identification are typically prepared by coating the sensory materials on planar substrates (Figure 1, top). Some novel strategies have been employed to improve the sensor performance, such as extending the exciton diffusion length,<sup>25</sup> enlarging the surface area for interaction<sup>26,27</sup> and utilizing optical modulation.<sup>5</sup> Though enhanced sensitivity was achieved by stimulated emission in waveguides,<sup>5</sup> the emission was directional along the gain regime, which confined the detection flexibility; moreover, its preparation process was considerably complex and costly. In our contribution, the advantages of low cost and easy fabrication were apparent. Also, the multidirectional lasing emission of the random laser facilitated the sensory signal detection.

For lasing in organic solids, the polymer material could be treated as a standard four-level laser system (see Supporting Information, Figure S2):<sup>18</sup> (1) the electronic and geometric ground state of the polymer, (2) the electronic ground state and the nuclear excited state, (3) the electronic excited state and nuclear ground state, and (4) the electronic and nuclear excited state of the polymer.<sup>5</sup> From 1 to 4 is in the order of increasing

energy. From the analysis, we could export the sensitivity of lasing, in terms of the fractional change in the output power:

$$\frac{\Delta I}{I} = \frac{P_{\text{laser}} - P_{\text{laser}}'}{P_{\text{laser}}} = \frac{(P_{\text{pump}} - P_{\text{th}})(P_{\text{pump}} - P_{\text{th}}')}{P_{\text{pump}} - P_{\text{th}}} = \frac{(\beta - 1)P_{\text{th}}}{P_{\text{pump}} - P_{\text{th}}} \quad (1)$$

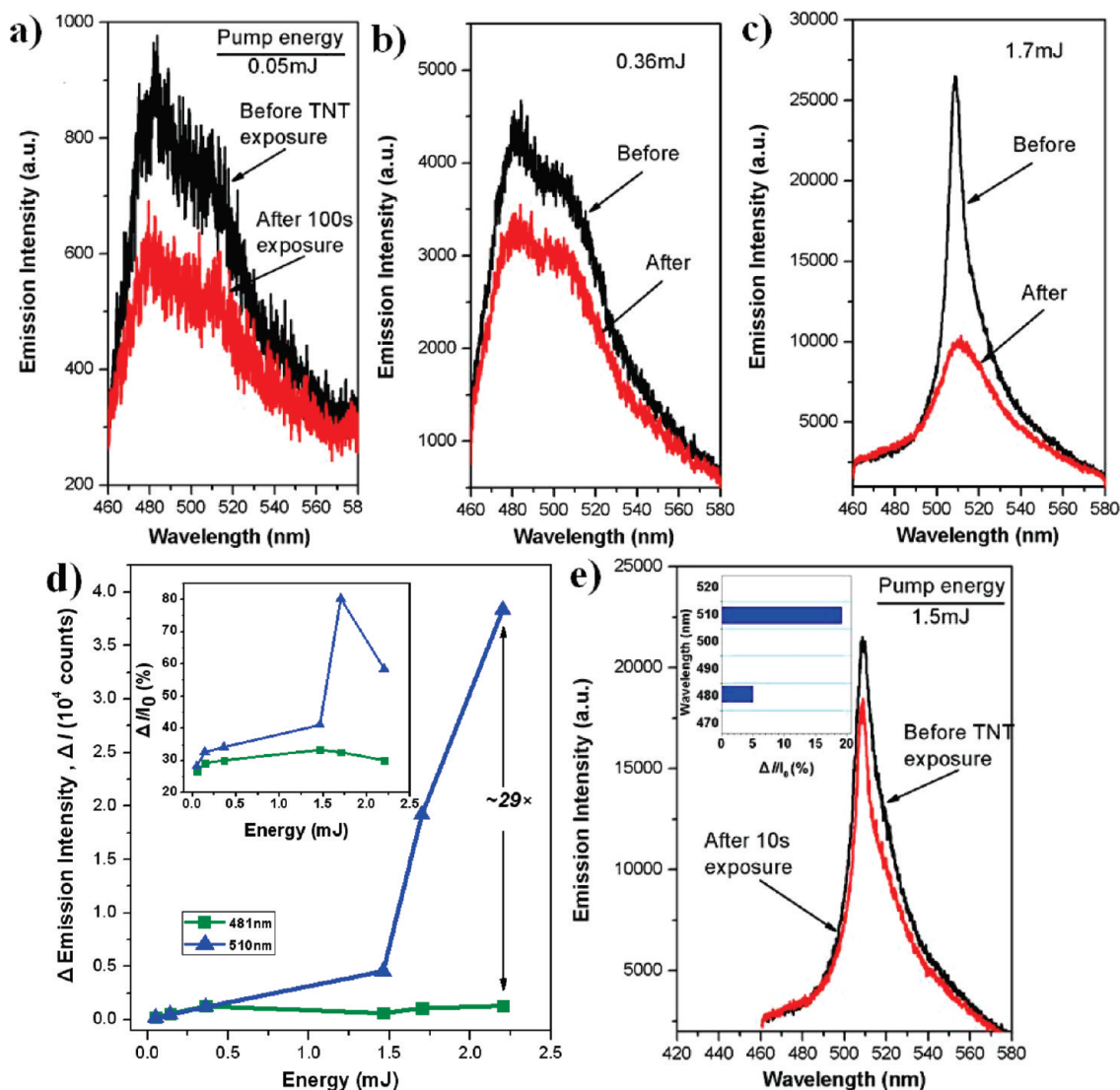
We could also obtain the traditional sensitivity of fluorescent in presence of TNT:

$$\frac{\Delta I}{I} = \frac{P_{\text{fluo}} - P_{\text{fluo}}'}{P_{\text{fluo}}} = \frac{P_{\text{pump}}R_{32}^{-1}A_{32} - P_{\text{pump}}R_{32}'^{-1}A_{32}}{P_{\text{pump}}R_{32}^{-1}A_{32}} = \frac{\beta - 1}{\beta} \quad (2)$$

where  $\beta = R_{32}'/R_{32}$  (see Supporting Information, Figure S3),  $P_{\text{pump}}$  is the pump power of laser, and  $p_{\text{th}}$  and  $p_{\text{th}}'$  are the threshold pump power before and after introducing TNT, respectively. In eq 2,  $A_{32}$  represents the rate of spontaneous radiative relaxation in SOPs. Now compare (1) with (2), due to  $\beta > 1$ , we can set  $\beta = 1.5$ , then the traditional sensitivity can be 33.3%. When the pump power is 1.5-fold the threshold of lasing, the quenching efficiency could be 100%. We find that the threshold of lasing is increased after introducing TNT, which depletes the populations of the upper level of the laser. Another conclusion shows that detection sensitivity depends on the pump power; in other words, the highest sensitivity could be achieved when the pump power is close to the threshold of lasing. It is evident that stimulated emission, which is essence of random lasing, improves the response performance and enhances the sensitivity compared to spontaneous emission, the essence of fluorescence.

#### 4. Conclusions

In conclusion, we have demonstrated that a random laser action generated from a SOP hybrid film containing TiO<sub>2</sub> nanoparticles can be used to enhance the sensitivity of the SOP



**Figure 6.** (a)–(c) Spectral response of optically pumped amplifying disordered film before and after a 100 s exposure to TNT (10 ppb). Approximate pulse energies  $E$  (in mJ): (a) 0.05; (b) 0.36; (c) 1.7 (d). Change in the output emission intensity,  $I$ , at  $\lambda = 481$  nm (spontaneous emission; olive squares) and  $\lambda = 510$  nm (random lasing; blue triangles) after 100 s TNT exposure versus pump power. Inset: quenching efficiency (%), that is, attenuation of intensity after exposure to TNT,  $\Delta I$ , divided by emission intensity before the exposure,  $I_0$ , as a function of pump energy. The largest response occurs near the threshold of lasing. (e), Spectral response of the same film before and after 10 s exposure to TNT at pump threshold (1.5 mJ), showing the sizable reduction in the lasing action emission with slight reduction in the spontaneous emission. Inset, quenching efficiency of spontaneous emission and lasing emission, shows the sensitivity enhancement of 4-fold in lasing action.

to TNT. The SOP in the hybrid film functions as both the gain medium and the sensory transducer. The hybrid film showed a high sensitivity to TNT vapor when a lasing measurement technique was employed with the excitation power close to or slightly higher than the lasing threshold. Due to the pump light in our system has unidirectional property compared to conventional light, such as a xenon lamp, so our sensor could be used to detect explosives from an even greater distance. Since the disordered system used in this work could replace the polymer with other functional materials, the concept developed could be extended to more general domains of chemical or environment detections. Current and future efforts focus on reducing the threshold of random lasing<sup>28</sup> and designing new functional materials with photostability.

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**Supporting Information Available:** Emission spectra. Description of enhanced sensitivity driven by random lasing action. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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