

# Low Dose Detection of $\gamma$ Radiation via Solvent Assisted Fluorescence Quenching

Ji-Min Han,<sup>†</sup> Miao Xu,<sup>†</sup> Brian Wang,<sup>‡</sup> Na Wu,<sup>†</sup> Xiaomei Yang,<sup>†</sup> Haori Yang,<sup>§</sup> Bill J. Salter,<sup>||</sup> and Ling Zang<sup>\*,†</sup>

<sup>†</sup>Department of Materials Science and Engineering, University of Utah, 36 South Wasatch Drive, Salt Lake City, Utah 84112, United States

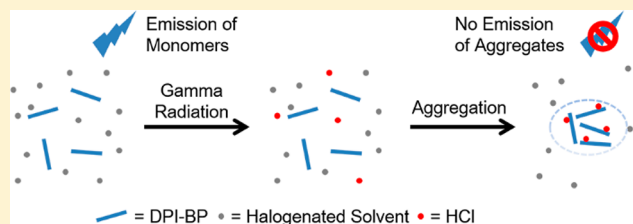
<sup>§</sup>Department of Nuclear Engineering & Radiation Health Physics, Oregon State University, 3451 SW Jefferson Way, Radiation Center E108, Corvallis, Oregon 97331, United States

<sup>‡</sup>Department of Radiation Oncology, University of Louisville, 529 South Jackson Street, Louisville, Kentucky 40202, United States

<sup>||</sup>Huntsman Cancer Institute, Department of Radiation Oncology, University of Utah, 1950 Circle of Hope, Salt Lake City, Utah 84112, United States

## Supporting Information

**ABSTRACT:** Development of low cost, easy-to-use chemical sensor systems for low dose detection of  $\gamma$  radiation remains highly desired for medical radiation therapy and nuclear security monitoring. We report herein on a new fluorescence sensor molecule, 4,4'-di(1*H*-phenanthro[9,10-*d*]imidazol-2-yl)-biphenyl (DPI-BP), which can be dissolved into halogenated solvents (e.g., CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>) to enable instant detection of  $\gamma$  radiation down to the 0.01 Gy level. The sensing mechanism is primarily based on radiation induced fluorescence quenching of DPI-BP. Pristine DPI-BP is strongly fluorescent in halogenated solvents. When exposed to  $\gamma$  radiation, the halogenated solvents decompose into various radicals, including hydrogen and chlorine, which then combine to produce hydrochloric acid (HCl). This strong acid interacts with the imidazole group of DPI-BP to convert it into a DPI-BP/HCl adduct. The DPI-BP/HCl adduct possesses a more planar configuration than DPI-BP, enhancing the  $\pi$ - $\pi$  stacking and thus molecular aggregation. The strong molecular fluorescence of DPI-BP gets quenched upon aggregation, due to the  $\pi$ - $\pi$  stacking interaction (forming forbidden low-energy excitonic transition). Interestingly the quenched fluorescence can be recovered simply by adding base (e.g., NaOH) into the solution to dissociate the DPI-BP/HCl adduct. Such sensing mechanism was supported by systematic investigations based on HCl titration and dynamic light scattering measurements. To further confirm that the aggregation caused fluorescence quenching, a half size analogue of DPI-BP, 2-phenyl-1*H*-phenanthro[9,10-*d*]imidazole (PI-Ph), was synthesized and investigated in comparison with the observations of DPI-BP. PI-Ph shares the same imidazole conjugation structure with DPI-BP and is expected to bind the same way with HCl. However, PI-Ph did not show fluorescence quenching upon binding with HCl likely due to the smaller  $\pi$ -conjugation structure, which can hardly enforce the  $\pi$ - $\pi$  stacking assembly. Combining the low detection limit, fast and reversible fluorescence quenching response, and low cost of halogenated solvent composites, the sensor system presented may lead to the development of new, simple chemical dosimetry for low dose detection of  $\gamma$  radiation.



## INTRODUCTION

Low dose detection of  $\gamma$  radiation remains essential in medical radiation treatment of cancer and for nuclear relevant security.<sup>1</sup> For example, the use of  $\gamma$  rays to treat cancerous tumors requires the precise calibration and delivery of  $\gamma$  radiation intensity (dose) to the tumor, for which the source intensity must be controlled down to the resolution of 0.01 Gy. Meanwhile, greater awareness of the threat of nuclear and radiological terrorism has been raised as a result of the growing violence in terrorist attacks. It becomes more critical now than ever to develop facile and low cost dosimeters for instant detection of  $\gamma$  radiation.

Current popular radiation dosimeters include ion chambers, semiconductor detectors, radiographic films, and scintillation

detectors. However, ion chambers are vulnerable to low sensitivity,<sup>2</sup> and semiconductor detectors suffer from energy and angular dependence.<sup>3</sup> The measured data by film-based detectors are time-consuming to read out. The single-crystal-based scintillation detectors are usually too costly to scale up.<sup>4</sup> To overcome these challenges, various organic chemical sensors (e.g., those based on molecules or polymers) have been developed and studied for gamma detection. Molecular and polymeric sensors provide many advantages over the current detector systems, including ease of processing, low cost, high adaptability for size miniaturization, and high conformability for

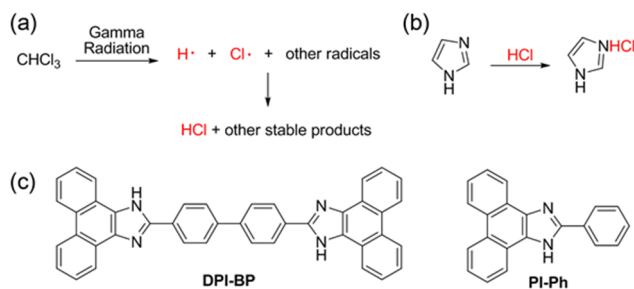
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fabrication into various shapes.<sup>5</sup> While many types of chemical sensors have been developed,<sup>6</sup> the best sensor system available so far can only detect  $\gamma$  radiation down to a level of about 10 Gy,<sup>6g,h</sup> still several orders of magnitude less sensitive than what is required for practical use in personnel dose monitoring or environmental radiation measurement. There is a large technical gap between laboratory research of chemical sensor systems and the practical application of such systems. We report herein on a new molecular sensor system that can significantly improve the detection limit by 3 orders of magnitude, down to 0.01 Gy.

Scheme 1 shows the molecular structure of the sensor, 4,4'-di(1*H*-phenanthro[9,10-*d*]imidazol-2-yl)biphenyl (DPI-BP),

**Scheme 1. (a) Generation of HCl from CHCl<sub>3</sub> under  $\gamma$  Radiation, (b) Formation of Imidazole/HCl Adduct in Nonpolar Solvents, and (c) Molecular Structures of the Sensor Molecule, DPI-BP, and Its Half Size Analogue, PI-Ph**



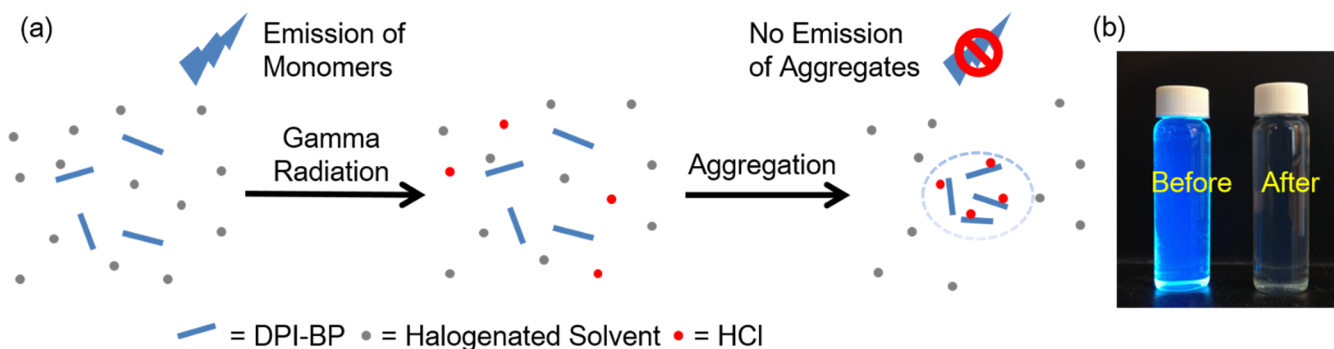
and the sensing mechanism based on  $\gamma$  radiation initiated radical reactions. The half size analogue of the sensor molecule, 2-phenyl-1*H*-phenanthro[9,10-*d*]imidazole (PI-Ph), was also synthesized and used as a reference to study the sensing mechanism. Under  $\gamma$  radiation, the halogenated solvents, such as chloroform (CHCl<sub>3</sub>) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), decompose into free radicals as shown in Scheme 1a.<sup>7</sup> These radicals are unstable, undergoing fast recombination to form new compounds including hydrochloric acid (HCl). The presence of water (humidity) and oxygen under ambient condition does not affect significantly the production of HCl, mainly due to their slow reaction with the radicals.<sup>8</sup> This inspired us to develop a sensing pathway that can detect  $\gamma$  radiation simply by detecting HCl thus produced. However, in situ detection of HCl in nonpolar solvents still remains a great challenge.<sup>9</sup> Current pH sensors, particularly those based on

fluorophores, can only detect protons in polar solvents (e.g., water, DMSO),<sup>10</sup> whereas in nonpolar solvents HCl can hardly be ionized into free protons. To overcome this technical challenge, we have herein developed a new fluorescence sensor molecule, DPI-BP, which can dissolve into halogenated solvents to enable instant sensing of HCl generated under  $\gamma$  radiation (Figure 1). The sensing mechanism is primarily based on the addition reaction between HCl and the imidazole moieties of DPI-BP. The HCl adduct of DPI-BP intends to aggregate, causing quenching of the molecular fluorescence of DPI-BP due to the intermolecular  $\pi$ - $\pi$  stacking interaction.

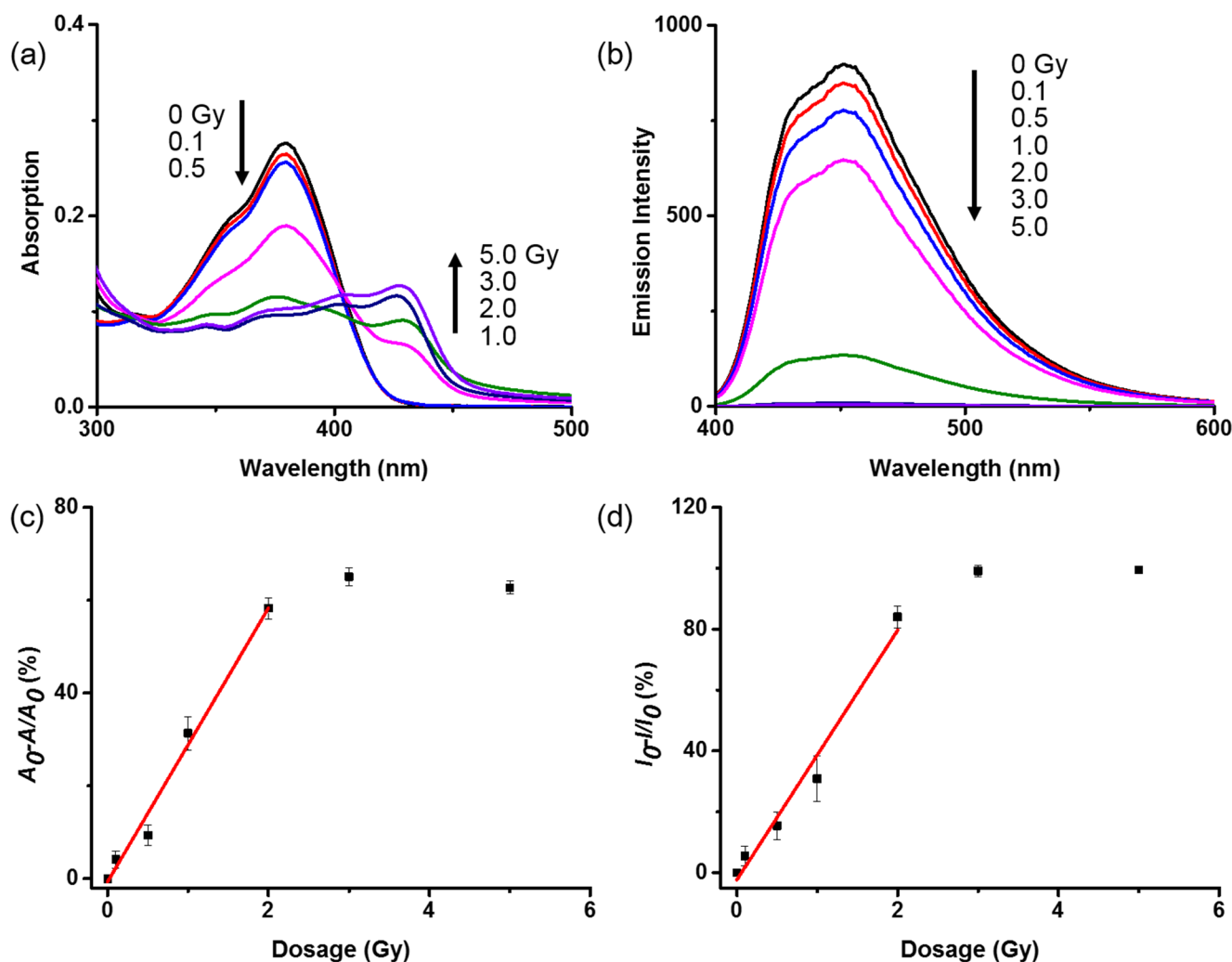
The design of DPI-BP was based on 3-fold consideration. First, the imidazole moiety has been widely employed in synthesis of organic semiconducting materials,<sup>11</sup> because of its ease for structure modification,<sup>12</sup> strong chemical durability<sup>13</sup> and high fluorescence efficiency of the  $\pi$ -conjugated system.<sup>14</sup> Indeed, DPI-BP was synthesized in this work with a high yield of 90%, and its fluorescence quantum yield ( $\Phi$ ) was determined to be as high as 0.81 (see Supporting Information). Second, as common alkaloid heterocycles, the  $\pi$ -expanded derivatives of imidazole have high affinity to acids;<sup>15</sup> thus they form a stable adduct with HCl instantly in nonpolar solvents. Lastly, the decreased solubility of the DPI-BP/HCl adduct, in conjunction with the strong intermolecular  $\pi$ - $\pi$  stacking interaction, leads to aggregation of DPI-BP molecules, which in turn results in effective fluorescence quenching of the molecules.<sup>16</sup> To confirm the aggregation induced fluorescence quenching, we have synthesized a reference compound, PI-Ph, a half sized analogue of DPI-BP (Scheme 1), and investigated it for  $\gamma$  radiation sensing following the same procedures as those tested for DPI-BP. As expected, due to the smaller size (and thus the higher solubility) of PI-Ph, no aggregation was observed for this compound when interacting with HCl. Combining the low detection limit and expedient sensing response (via rapid radical reactions), the reported sensor system of DPI-BP will help open new opportunities for developing low-cost, easy-to-use devices for low dose detection of  $\gamma$  radiation.

## MATERIALS AND METHODS

PI-Ph was synthesized following the literature methods.<sup>12a</sup> DPI-BP was synthesized as follows: Phenanthrene-9,10-quinone (1.0 g, 4.8 mmol), ammonium bicarbonate (5.0 g, 63 mmol, excess), and biphenyl-4,4'-dicarbaldehyde (0.5 g, 2.4 mmol) were added into 150 mL of EtOH in a 250 mL round flask; the suspension thus obtained was refluxed for 6 h. During the refluxing, bright yellow precipitate was eventually



**Figure 1.** (a) Schematic drawing of the fluorescence sensing mechanism of DPI-BP. Protonation interaction with radiation generated HCl causes molecular aggregation of DPI-BP, which in turn results in fluorescence quenching due to  $\pi$ - $\pi$  stacking. (b) Fluorescence photograph of a DPI-BP solution in CHCl<sub>3</sub> taken before (left) and after (right) 3.0 Gy of  $\gamma$  radiation, indicating complete fluorescence quenching.



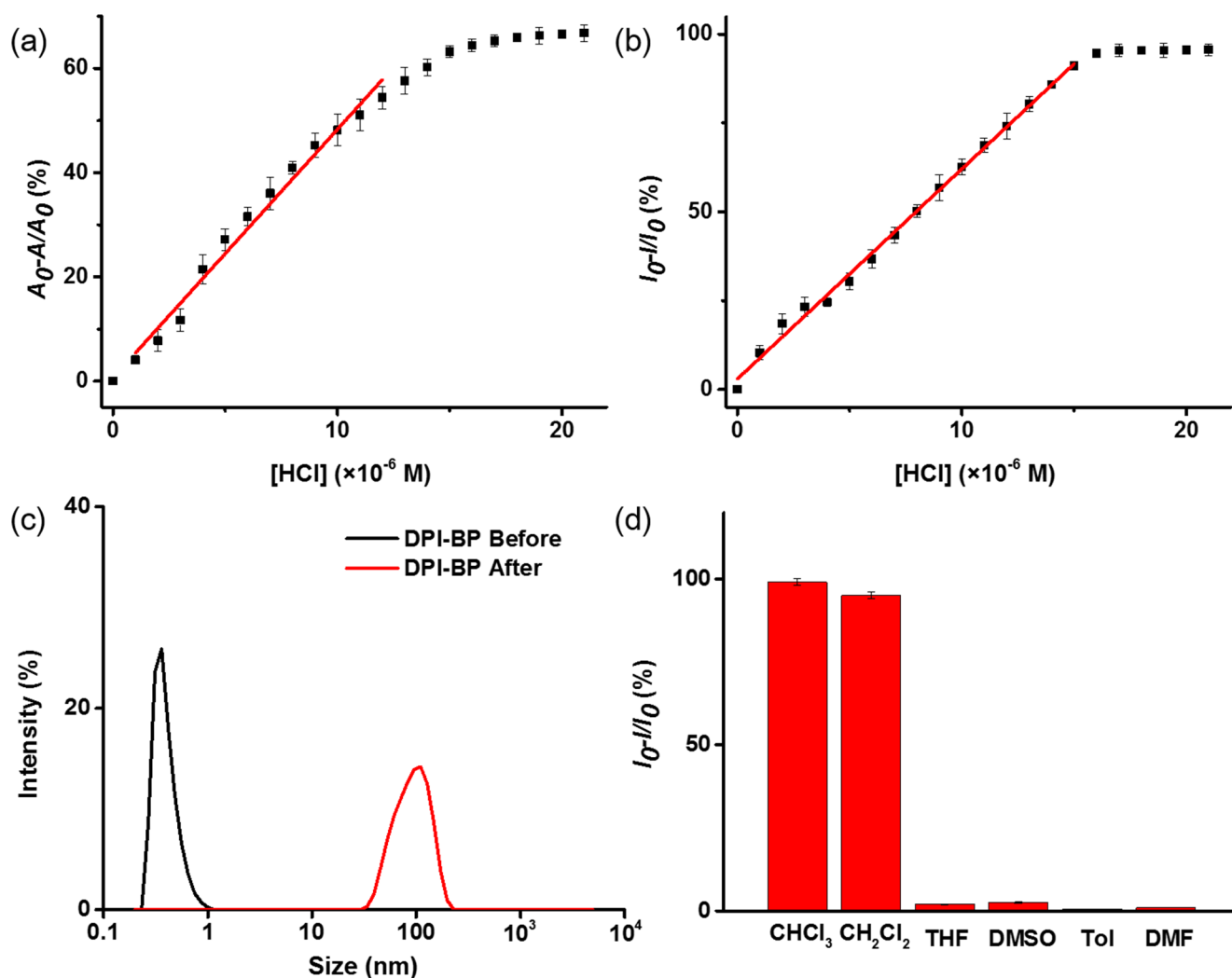
**Figure 2.** (a) Absorption and (b) fluorescence spectra of a  $\text{CHCl}_3$  solution of DPI-BP ( $5 \times 10^{-6}$  mol/L) recorded under increasing doses of  $\gamma$  radiation up to 5.0 Gy. (c) A plot showing the relative decrease in absorption (measured at 378 nm) of the same DPI-BP solution shown in panel a as a function of the dosage of  $\gamma$  radiation; the data points in low dosage range (0–2.0 Gy) are fitted in linear relationship ( $R^2 = 0.988$ ). (d) A plot showing the relative fluorescence quenching (measured at 451 nm) of the same DPI-BP solution shown in panel b as a function of the dosage of  $\gamma$  radiation; the data points in low dosage range (0–2.0 Gy) are fitted in linear relationship ( $R^2 = 0.980$ ).

formed. After cooling to room temperature, the mixture was filtered, and the residue was collected. The crude product was then washed with deionized water ( $2 \times 25$  mL), ethanol ( $2 \times 25$  mL), and cold  $\text{CHCl}_3$  ( $2 \times 25$  mL), and finally dried under vacuum. The final product of DPI-BP was obtained as a yellow solid (1.27 g, 90% yield).  $^1\text{H}$  NMR (DMSO- $d_6$ , 300 MHz, ppm):  $\delta = 13.66$  (2 H, s), 8.90 (4 H, d,  $J = 8$  Hz), 8.65 (4 H, d,  $J = 8$  Hz), 8.5 (4 H, d,  $J = 8$  Hz), 8.11 (4 H, d,  $J = 8$  Hz), 8.79 (4 H, t,  $J = 8$  Hz), 8.68 (4 H, t,  $J = 8$  Hz).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 75 MHz, ppm):  $\delta = 149.6$ , 140.6, 130.5, 128.5, 128.0, 127.9, 127.6, 126.2, 124.8, 122.9. LRMS (ESI):  $m/z$  calcd 586.2; found 587.2  $[\text{M} + \text{H}]^+$ .

Halogenated methanes are commonly used for radical generation under radiation, with the efficiency in the order of  $\text{CH}_2\text{I}_2 > \text{CHBr}_3 > \text{CH}_2\text{Br}_2 > \text{CHCl}_3 > \text{CH}_2\text{Cl}_2$ .<sup>17</sup> Considering the fact that DPI-BP is not fluorescent in iodinated and brominated solvents due to the enhanced intersystem crossing (ISC) by the so-called “heavy-atom effect”,<sup>18</sup> we chose  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  as the two major solvents to study the sensor reactions. Though halogenated ethanes and other larger alkanes may function similarly regarding radical generation, these solvents were not employed for testing mainly because of their decreased efficiency in production of hydrogen halides.  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  were purchased from Sigma-Aldrich. Before being used for experiments, these solvents were further purified to remove the excessive acids and stabilizers. Briefly,  $\text{CHCl}_3$  (200 mL) was washed with deionized water

(200 mL) to remove EtOH and HCl, followed by drying with  $\text{CaCl}_2$ . After refluxing with  $\text{P}_2\text{O}_5$ , the  $\text{CHCl}_3$  was collected by distillation.  $\text{CH}_2\text{Cl}_2$  (200 mL) was then refluxed with  $\text{CaH}_2$  and collected by distillation. The purified  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  thus obtained were sealed and stored in the dark to avoid photochemical decomposition.

$\gamma$ -Irradiation experiments were performed with a 6 MV photon beam on a Varian/BrainLab Novalis Classic (Varian Medical Systems, Palo Alto, CA; BrainLAB AG, Feldkirchen, Germany) linear accelerator (LINAC) at room temperature. The radiation output was calibrated by an ionization chamber to generate 0.01 Gy/MU (monitor unit) at maximum dose depth of 1.4 cm in water with a source to surface distance (SSD) of 100 cm. The ionization chamber used has a calibration that is traceable to an accredited dosimetry calibration laboratory. The radiation beam from the LINAC machine head was angled to the downward direction, wherein the sensor samples were placed underneath at a height that was calculated to yield a specific dose of radiation. Slabs of solid water were placed atop the samples to provide dose building up. Before exposure to  $\gamma$  radiation, the  $\text{CHCl}_3$  solution of DPI-BP was colorless, with strong blue fluorescence (Figure 1b). Upon irradiation of 3.0 Gy, the fluorescence of DPI-BP was completely quenched, implying instant sensor response for  $\gamma$  radiation.



**Figure 3.** (a) A plot showing the relative decrease in absorption (measured at 378 nm) of a  $CHCl_3$  solution of DPI-BP ( $5 \times 10^{-6}$  mol/L) as a function of the concentration of HCl added; the data points in low concentration range ( $(0-15) \times 10^{-6}$  mol/L) are fitted in linear relationship ( $R^2 = 0.987$ ). (b) A plot showing the relative fluorescence quenching (measured at 451 nm) of the same DPI-BP solution shown in panel a as a function of the concentration of HCl added; the data points in low concentration range ( $(0-15) \times 10^{-6}$  mol/L) are fitted in linear relationship ( $R^2 = 0.991$ ). (c) Result of dynamic light scattering measured over a  $CHCl_3$  solution of DPI-BP ( $5 \times 10^{-6}$  mol/L) before and after 3.0 Gy of  $\gamma$  radiation. (d) Comparison of the fluorescence quenching efficiency of DPI-BP ( $5 \times 10^{-6}$  mol/L) dissolved in  $CHCl_3$  and  $CH_2Cl_2$  upon 3.0 Gy of  $\gamma$  radiation; also compared are the results of the same concentration of DPI-BP dissolved in several other nonhalogen solvents, though upon 100 Gy of  $\gamma$  radiation.

## RESULTS AND DISCUSSION

The halogenated solvent mediated  $\gamma$  radiation sensor system was investigated in detail using both UV-vis absorption and fluorescence spectral measurements. As shown in Figure 2a, the main absorption peak of DPI-BP centered at 378 nm decreased gradually with increasing dose of  $\gamma$  radiation. Meanwhile, a new absorption band emerged around 428 nm, corresponding to the formation of DPI-BP/HCl adduct. Along with this new absorption band, the absorption baseline at the longer wavelength was also increased, indicating the formation of molecular aggregation that caused light scattering. The electronic structure of DPI-BP before and after binding with HCl was calculated by using time dependent density functional theory (TD-DFT) (see Supporting Information). For pristine DPI-BP, the energy band gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels is calculated as 3.40 eV, which matches the absorption peak measured at 378 nm. The band gap of the DPI-BP/HCl adduct is calculated to be 3.10 eV, which is also

consistent with the new absorption band measured at 428 nm. More strikingly, the optimized (energy minimized) structure of DPI-BP/HCl adduct showed approximately coplanar configuration, that is, only ca.  $11^\circ$  between the two BPI planes (Figure S2, Supporting Information). In contrast, the pristine DPI-BP demonstrates a typical twisted configuration between the two BPI planes, with a torsional angle as large as  $47^\circ$  (Figure S1, Supporting Information). The coplanar geometry of DPI-BP/HCl adduct is highly conducive to the cofacial intermolecular  $\pi-\pi$  stacking.<sup>5d</sup> The calculation result supports the hypothesis that binding with HCl enhances the molecular aggregation of DPI-BP, which is also consistent with the increased light scattering observed at longer wavelength (Figure 2a). As to be demonstrated below, the dynamic light scattering measurement also confirmed the formation of aggregation of DPI-BP upon binding with HCl.

Parallel with the absorption measurement, the fluorescence spectra of the same  $CHCl_3$  solution of DPI-BP was also measured as shown in Figure 2b. Before exposure to  $\gamma$

radiation, the DPI-BP solution demonstrated strong blue emission with maximal wavelength centered at 451 nm. Upon  $\gamma$  irradiation, the emission intensity was gradually quenched with increase in radiation dosage. Remarkably, after only 0.1 Gy of  $\gamma$  radiation exposure, the emission of DPI-BP decreased about 5.5%. Such significant fluorescence quenching implies great potential of the DPI-BP sensor for low dose detection. Continuous exposure to radiation up to 3.0 Gy resulted in complete fluorescence quenching of the DPI-BP solution. Figure 2c,d presents the change of absorption and fluorescence intensity (data obtained from Figure 2a,b, respectively) as a function of the  $\gamma$  radiation dose. Both plots show a linear relationship in the low dose range (0 to 2.0 Gy), which provides quite wide dynamic range for quantitative analysis of the detection limit. If we define a decrease in spectral intensity three times higher than the standard deviation as the detectable signal, the detection limit for the DPI-BP sensor system shown in Figure 2 is projected to be ca. 0.01 Gy (by using the absorption data) or 0.007 Gy (by using fluorescence data) (see Supporting Information). The detection limit thus projected is about 3 orders of magnitude better than those previously reported for the other organic or polymeric fluorescence sensors.<sup>6g,h</sup> Moreover, the DPI-BP sensor can be completely recovered after exposure to  $\gamma$  radiation simply by adding strong base, such as NaOH or Et<sub>3</sub>N (Figure S9, Supporting Information), which deprotonates the HCl from the DPI-BP/HCl adduct, thus dissolving the aggregate back to molecular solution of free base DPI-BP. Both absorption and fluorescence spectra were measured for this recovered DPI-BP solution and showed no difference compared with the original solution before  $\gamma$  radiation. This observation also helps confirm the critical role of HCl in the sensing process of DPI-BP as outlined in Scheme 1 and Figure 1. The reversibility, together with the high sensitivity and fast response, thus obtained for the DPI-BP solution makes it an ideal sensor system for expedient detection of  $\gamma$  radiation.

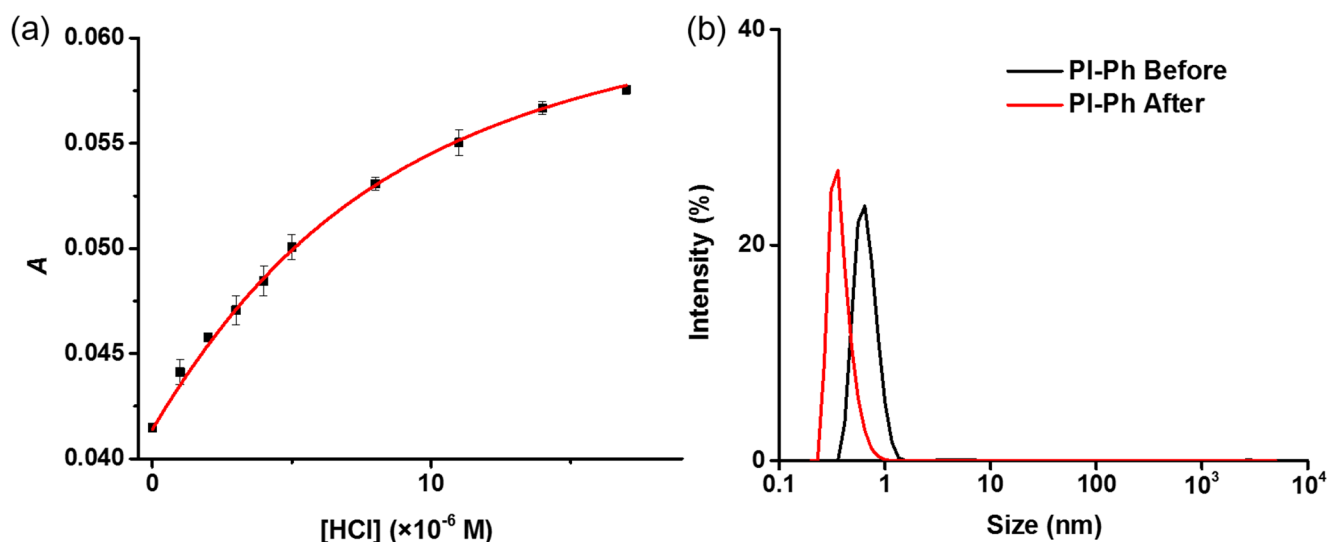
To further prove that the above observed fluorescence quenching of DPI-BP was induced by the radiation generated HCl acid, a series of titration experiments were conducted within the same DPI-BP solution in CHCl<sub>3</sub>. As expected, upon addition of HCl, both the absorption and fluorescence spectra of DPI-BP (Figure S3, Supporting Information) underwent almost identical spectral change as obtained under  $\gamma$  radiation (Figure 2a,b). Moreover, the fluorescence quenching was observed instantly upon titration with HCl, indicating the expedient acid–base interaction between HCl and the imidazole moiety of DPI-BP. We also examined the same titration process by replacing DPI-BP with a conventional fluorescent pH sensor based on rhodamine. Since the rhodamine sensor only reacts with free protons and HCl can hardly be ionized into free protons in hydrophobic solvent like CHCl<sub>3</sub>, the presence of HCl in CHCl<sub>3</sub> solution (10<sup>-5</sup> mol/L) did not turn on the fluorescence of rhodamine molecules (5 × 10<sup>-6</sup> mol/L) (Figure S4, Supporting Information). In contrast, when the same experiment was repeated in 1:1 (volume) water/ethanol solvent (where free protons are available), significant fluorescence turn-on of rhodamine was observed. When the concentration of HCl in CHCl<sub>3</sub> solution was increased to 10<sup>-4</sup> mol/L (i.e., 20 times excess of the concentration of rhodamine), the fluorescence could still just barely be activated, and the increase in emission intensity took over 500 min to reach equilibrium, indicating the slow protonation process of rhodamine sensor in hydrophobic

solvent (Figure S5, Supporting Information). Even at equilibrium, the emission intensity observed was only about one-third of the intensity observed in the hydrophilic water/ethanol solvent, wherein the concentration of HCl was only two times that of the rhodamine sensor. Moreover, with the assumption that the fluorescence quenching of DPI-BP observed under  $\gamma$  radiation is solely due to the interaction with HCl, the titration curves shown in Figure 3a,b can be used to estimate the concentration of HCl formed under different doses of  $\gamma$  radiation. For instance, for 1 Gy of delivered  $\gamma$  radiation dose, the fluorescence of DPI-BP was quenched by 32%, which corresponds to 6.0 × 10<sup>-6</sup> mol/L of HCl (as shown in Figure 3b). This concentration is in good agreement with the theoretically projected value,<sup>7b</sup> 8.0 × 10<sup>-6</sup> mol/L of HCl produced under 1.0 Gy of delivered  $\gamma$  radiation. In addition to HCl, other molecules may also be formed under the  $\gamma$  radiation through recombination of the radicals produced (Scheme 1). These new molecules may include tetrachloromethane, pentachloroethane, 1,1,2,2-tetrachloroethane, and tetrachloroethene. To exclude the possibility that the observed fluorescence quenching above was due to these byproducts, we also performed the fluorescence titration experiments of the same DPI-BP solution in CHCl<sub>3</sub> (as used in Figure 3) by adding the four molecules. The results showed that none of these molecules caused significant fluorescence quenching of the sensor even when the concentration added was increased up to 5 × 10<sup>-4</sup> mol/L (Figure S8, Supporting Information). This is in sharp contrast to the titration result with HCl, for which close to 100% fluorescence quenching was achieved even when the concentration of HCl was as low as 1.5 × 10<sup>-5</sup> mol/L. Clearly the observed fluorescence quenching of DPI-BP is due to the binding reaction with HCl.

To confirm the molecular aggregation of DPI-BP upon interaction with HCl generated under  $\gamma$  radiation, dynamic light scattering (DLS) measurements were performed over the CHCl<sub>3</sub> solution of DPI-BP (5 × 10<sup>-6</sup> mol/L) before and after exposure to 3.0 Gy of  $\gamma$  radiation (Figure 3c). The hydrodynamic radius ( $R_h$ ) of DPI-BP before the  $\gamma$  irradiation has a narrow distribution below 1 nm, indicating that DPI-BP was molecularly dissolved in the CHCl<sub>3</sub> solution. In contrast, larger aggregates with wider range of size (averaged around 100 nm) were formed in the solution after  $\gamma$  irradiation, consistent with the discussion above that the DPI-BP/HCl adduct is more favored for molecular assembly through  $\pi$ – $\pi$  stacking.

To further explore the essential role of halogenated solvent in the radiation induced fluorescence quenching of DPI-BP, we also performed the same experiments in another halogenated solvent, CH<sub>2</sub>Cl<sub>2</sub>, and several other nonhalogenated solvents, such as THF, DMSO, toluene, and DMF (Figure 3d). As expected, the CH<sub>2</sub>Cl<sub>2</sub> solution demonstrated almost the same quenching efficiency as CHCl<sub>3</sub>, indicating the same radical reaction mechanism as shown in Scheme 1. However, no detectable fluorescence quenching was observed for all the nonhalogenated solvents, even under much higher dose of  $\gamma$  radiation, 100 Gy. This observation further supports the hypothesis that the sensing of DPI-BP relies on the radiation induced generation of HCl.

The design of the sensor molecule DPI-BP is also well justified regarding the expanded  $\pi$ -conjugation that is conducive to increasing the  $\pi$ – $\pi$  stacking interaction, thus leading to molecular aggregation. For comparison, we designed and synthesized a smaller analogue, PI-Ph, which possesses the same conjugation of DPI-BP but only half size and is suited for



**Figure 4.** (a) A plot showing the absorption change of PI-Ph ( $5 \times 10^{-6}$  mol/L  $\text{CHCl}_3$  solution) recorded at 356 nm as a function of the concentration of HCl added; data points are fitted with the bimolecular reaction equilibrium ( $R^2 = 0.995$ ). (b) DLS measurement over a  $\text{CHCl}_3$  solution of PI-Ph ( $5 \times 10^{-6}$  mol/L) before and after 5.0 Gy of  $\gamma$  radiation.

being used as a reference compound to study the sensing mechanism. When examined under the same experimental conditions (for both  $\gamma$  radiation and HCl titration in  $\text{CHCl}_3$  solution), PI-Ph underwent a very similar spectral shift, indicating the acid–base binding with HCl in both cases (Figures S6 and S7, Supporting Information). However, no fluorescence quenching was observed. The spectral change caused by HCl titration shows well-defined isosbestic points in both absorption and fluorescence spectra, indicating the stoichiometric transformation of PI-Ph to the PI-Ph/HCl adduct. The bathochromic shift of fluorescence observed for the PI-Ph/HCl adduct is consistent with our theoretical calculation and previous observation on similar imidazole based fluorophores.<sup>19</sup> The lack of fluorescence quenching is consistent with the smaller conjugation structure of PI-Ph, for which the  $\pi$ – $\pi$  stacking interaction is not as strong as that of DPI-BP to afford molecular aggregation. This was further confirmed by the DLS experiment performed on the  $\text{CHCl}_3$  solution of PI-Ph before and after 5.0 Gy of gamma irradiation (Figure 4b), wherein both the hydrodynamic radii  $R_h$  were smaller than 1 nm, indicating no molecular aggregation. To quantify the strong interaction between imidazole moiety and HCl in  $\text{CHCl}_3$ , we fit the titration data with bimolecular reaction equilibrium (Figure 4a), from which the binding constant of PI-Ph/HCl was estimated to be  $1.92 \times 10^5$  L/mol (see Supporting Information). This high value of binding constant implies effective formation of the PI-Ph/HCl adduct in diluted  $\text{CHCl}_3$  solution. Considering the same imidazole based structure of PI-Ph and DPI-BP, we speculate that the interaction of DPI-BP with HCl would share similar binding strength, though it undergoes multistep equilibrium because it contains two imidazole moieties. Combination of all the observations above clearly supports the hypothesis that the  $\gamma$  radiation induced fluorescence quenching of DPI-BP is mainly due to the binding interaction with HCl, which in turn causes molecular aggregation through  $\pi$ – $\pi$  stacking assembly.

## CONCLUSION

In conclusion, we have developed a fluorescence sensor molecule, DPI-BP, which can be dissolved in halogenated

solvents (e.g.,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ) to enable instant detection of  $\gamma$  radiation down to the 0.01 Gy level. The sensing mechanism is primarily based on fluorescence quenching of DPI-BP upon binding to HCl, forming DPI-BP/HCl adduct, which enhances the  $\pi$ – $\pi$  stacking interaction and thus the molecular aggregation in the halogenated solvents. HCl was produced from the  $\gamma$  radiation induced decomposition of  $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$  and the subsequent radical recombination. Such a sensing mechanism was extensively investigated and proven by comparative experiments between DPI-BP and its half size analogue, PI-Ph, under both  $\gamma$  radiation and HCl titration. The uniqueness of the reported sensor system lies in the design of DPI-BP, which undergoes molecular aggregation upon binding with HCl. This feature, in combination with the high reactivity of halogenated solvents toward  $\gamma$  radiation, enables the development of a solvent assisted fluorescence quenching sensor for low dose radiation detection. Given the high sensitivity, expedient response, and low cost, the DPI-BP sensor composite may find broad applications in nuclear relevant security monitoring and dosage calibration and measurement in the medical  $\gamma$  ray treatment of cancer.

## ASSOCIATED CONTENT

### Supporting Information

Materials, general instrumentations, and sensor testing in solutions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

LZANG@eng.utah.edu

### Notes

The authors declare no competing financial interest.

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