Supporting Information

For

Low Dose Detection of Gamma Radiation via Solvent Assisted Fluorescence Quenching

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1. Materials and general methods

All the starting materials and organic solvents were purchased from Sigma-Aldrich and used as received. The silica gel and TLC plates (Silicycle Ultrapure Silica Gels SIL-5554-7) were purchased from EMD Chemicals Inc. UV-vis absorption spectra were measured on a PerkinElmer Lambda 25 spectrophotometer or Agilent Cary 100. Fluorescence spectra were measured on a PerkinElmer LS 55 spectrophotometer or Agilent Eclipse spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 300 MHz Spectrometer at room temperature in appropriate deuterated solvents. All chemical shifts are reported in parts per million (ppm). ESI MS spectra were recorded on a Micromass Quattro II Triple Quadrupole Mass Spectrometer, and the solvent used was methanol. The in situ temperature-controlled dynamic light scattering (DLS) measurements were performed on a Malvern Zetasizer Nano ZS (Malvern, Herrenberg, Germany) under the scattering angle of 173° at the wavelength of 378 nm for DPI-BP, and 356 nm for PI-Ph, respectively. Results at the temperature of 298K were reported as the average of five measurements with standard deviations. All the radiation experiments were irradiated by 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.

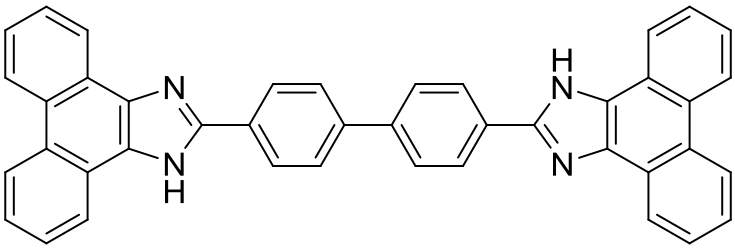
2. Fluorescence quantum yield measurement

Fluorescence quantum yield (Φ_s) of DPI-BP in chloroform solution was measured by using 9,10-diphenylanthracene (Φ_{std} = 0.91 in ethanol) as the standard. Value of Φ_s can be calculated according to Eq. (1), where I_s and I_{std} are the integrated emission intensities of the DPI-BP sample and the standard, respectively, A_s and A_{std} are the absorbance of the DPI-BP sample and the standard at the excitation wavelength, respectively, and η_s and η_{std} are the refractive indexes of the corresponding solutions (solvents).

$$\Phi_s = \Phi_{std} (I_s/ A_s) (A_{std}/ I_{std}) (\eta_s/ \eta_{std})^2 \quad (1)$$

3. Theoretical calculation

Geometry optimization and energy calculation of molecules were performed with density functional theory (B3LYP/6-311g**//B3LYP/6-31g*) using Gaussian 09 package.



DPI-BP

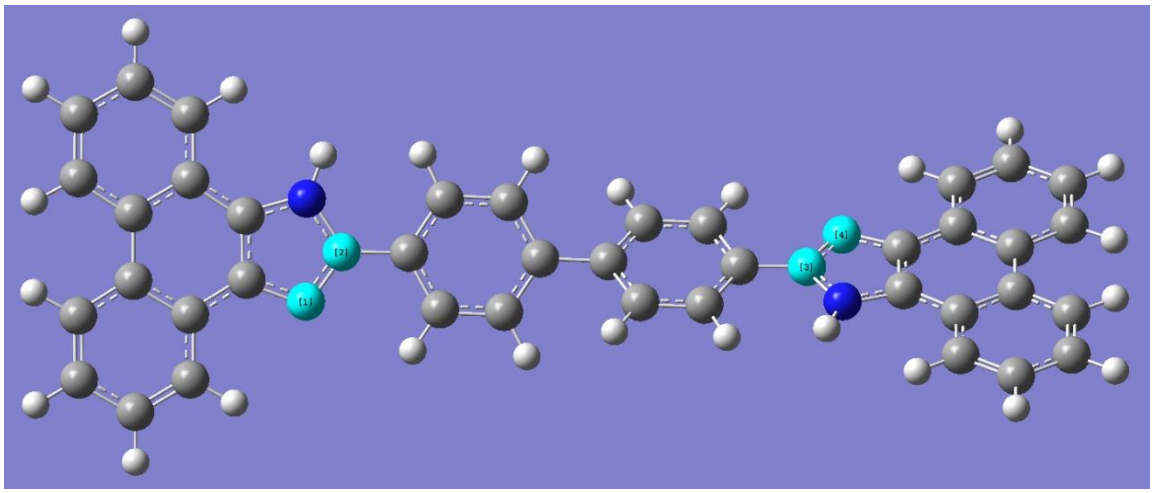
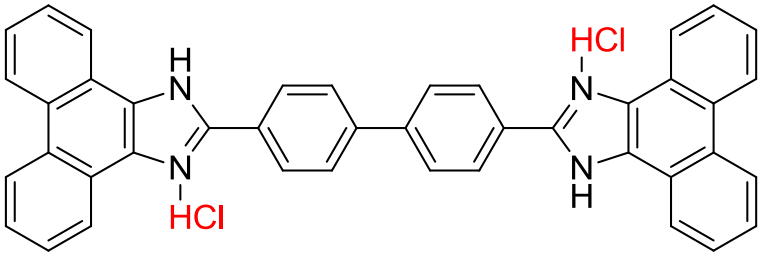


Figure S1. Energy minimized structure of DPI-BP, showing the strongly twisted, steric configuration. LUMO: -1.98 eV, HOMO: -5.38 eV, Gap: 3.4 eV.

Table S1 Dihedral Angles of DPI-BP

Groups	Dihedral Angles
BPI-BPI	133.4
BP-BP	143.9
BPI-BP	174.8



DPI-BP/HCl Adduct

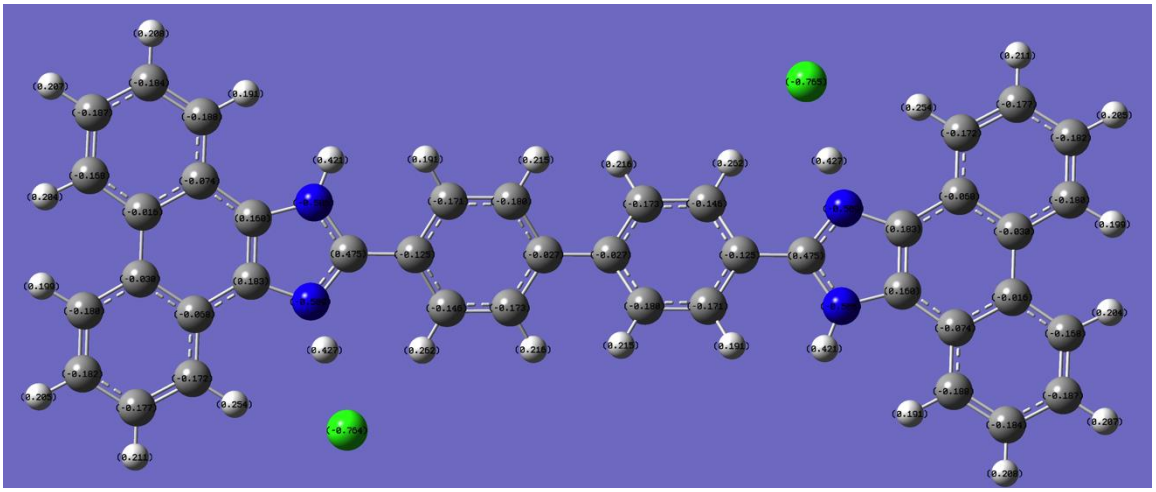


Figure S2. Energy minimized structure of DPI-BP/HCl adduct, showing almost co-planar configuration, favorable for π–π stacking. LUMO: -2.90 eV, HOMO: -6.0 eV, Gap: 3.1 eV.

Table S2 Dihedral Angles of DPI-BP/HCl Adduct

Groups	Dihedral Angles
BPI-BPI	168.6
BP-BP	144.8
BPI-BP	-167.7
BPI-BP	-168.2

4. Absorption and fluorescence spectral change of DPI-BP upon HCl titration

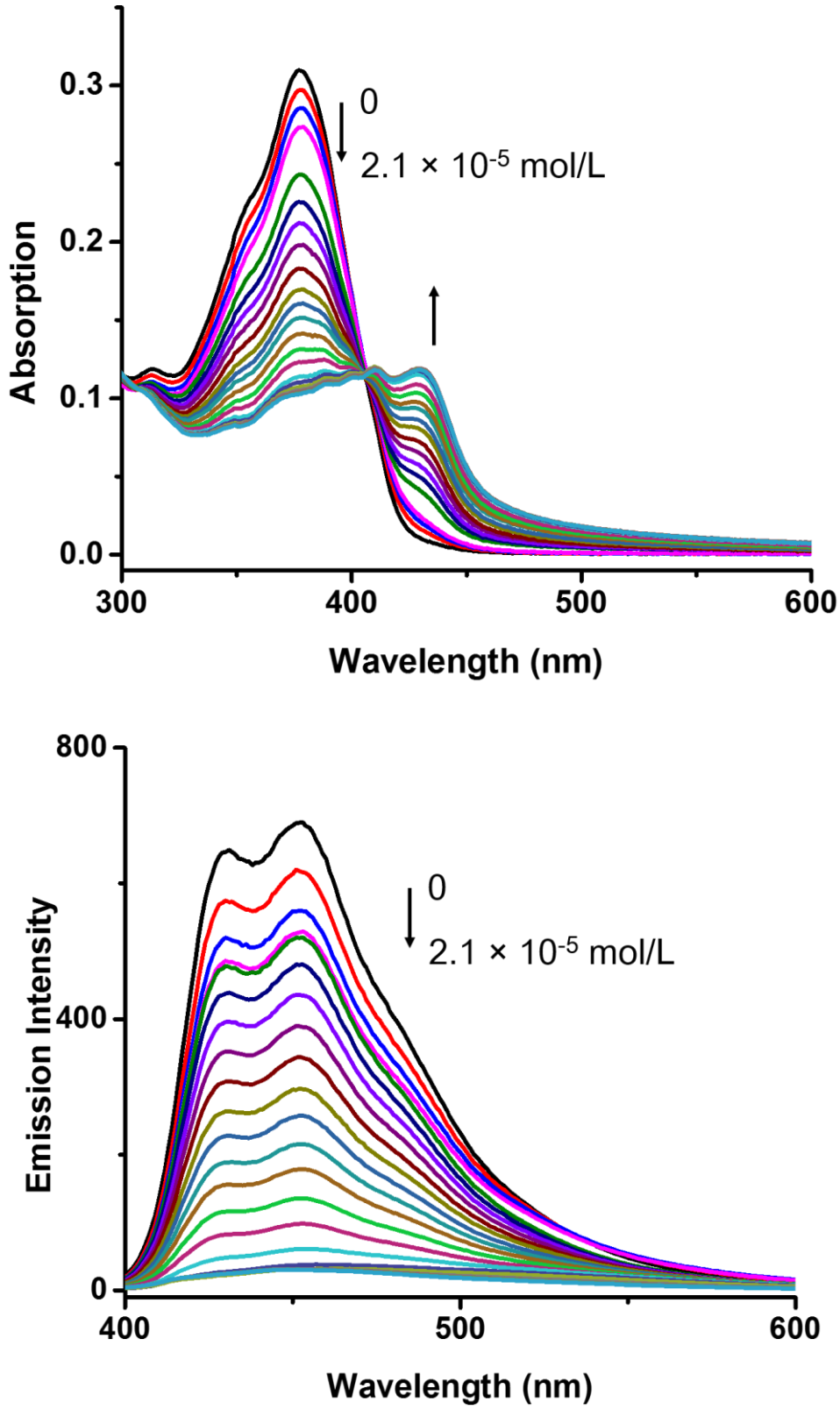
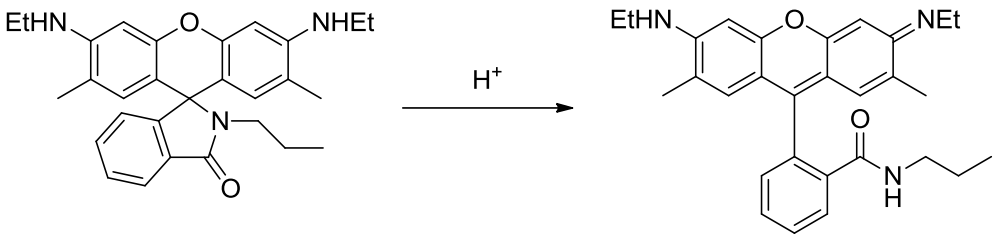


Figure S3. Absorption and fluorescent spectra of DPI-BP (5×10^{-6} mol/L $CHCl_3$ solution, 3.0 mL) upon

addition in the series of concentrations of HCl.

5. Fluorescence spectral change of Rhodamine pH sensor in different solvents



Rhodamine 1 **Rhodamine 2**

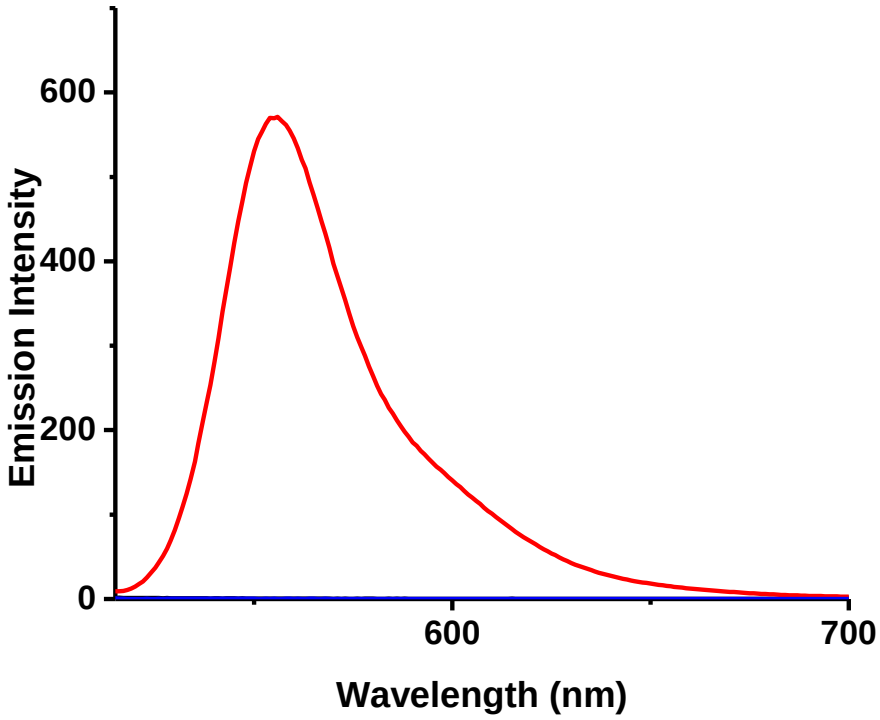


Figure S4. Fluorescence spectra of Rhodamine pH sensor (5×10^{-6} mol/L, 3.0 mL) in $CHCl_3$ (blue line) and 1:1 volume water:ethanol (red line) solution upon addition of 10^{-5} mol/L HCl (i.e., adding 15 μL of 2 mmol/L 1,4-dioxane solution of HCl). The spectra were recorded 1 min after addition of HCl.

6. Time dependent fluorescence intensity of Rhodamine pH sensor after addition of HCl

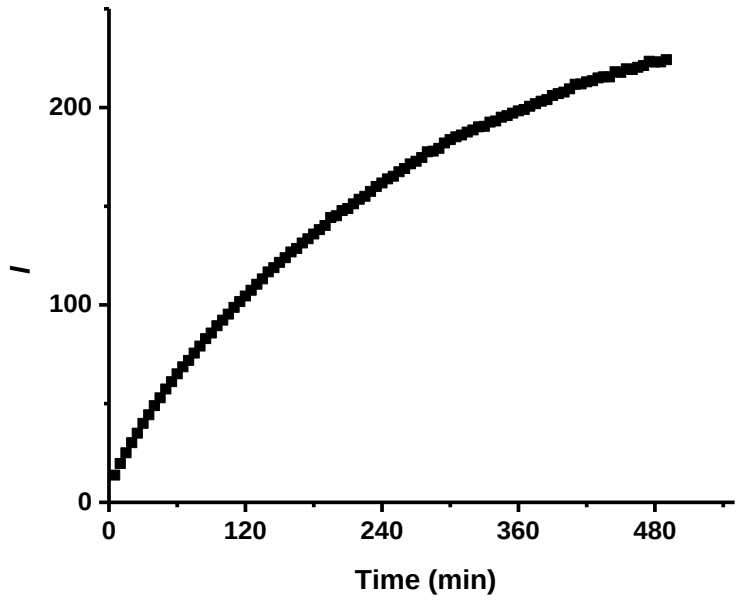


Figure S5. Time course of fluorescence intensity increase of Rhodamine pH sensor (5×10^{-6} mol/L in $CHCl_3$, 3.0 mL) after addition of 10^{-4} mol/L HCl (i.e., adding 15 μL of 20 mmol/L ethanol solution of HCl).

7. Absorption and fluorescence spectral change of PI-Ph upon gamma radiation

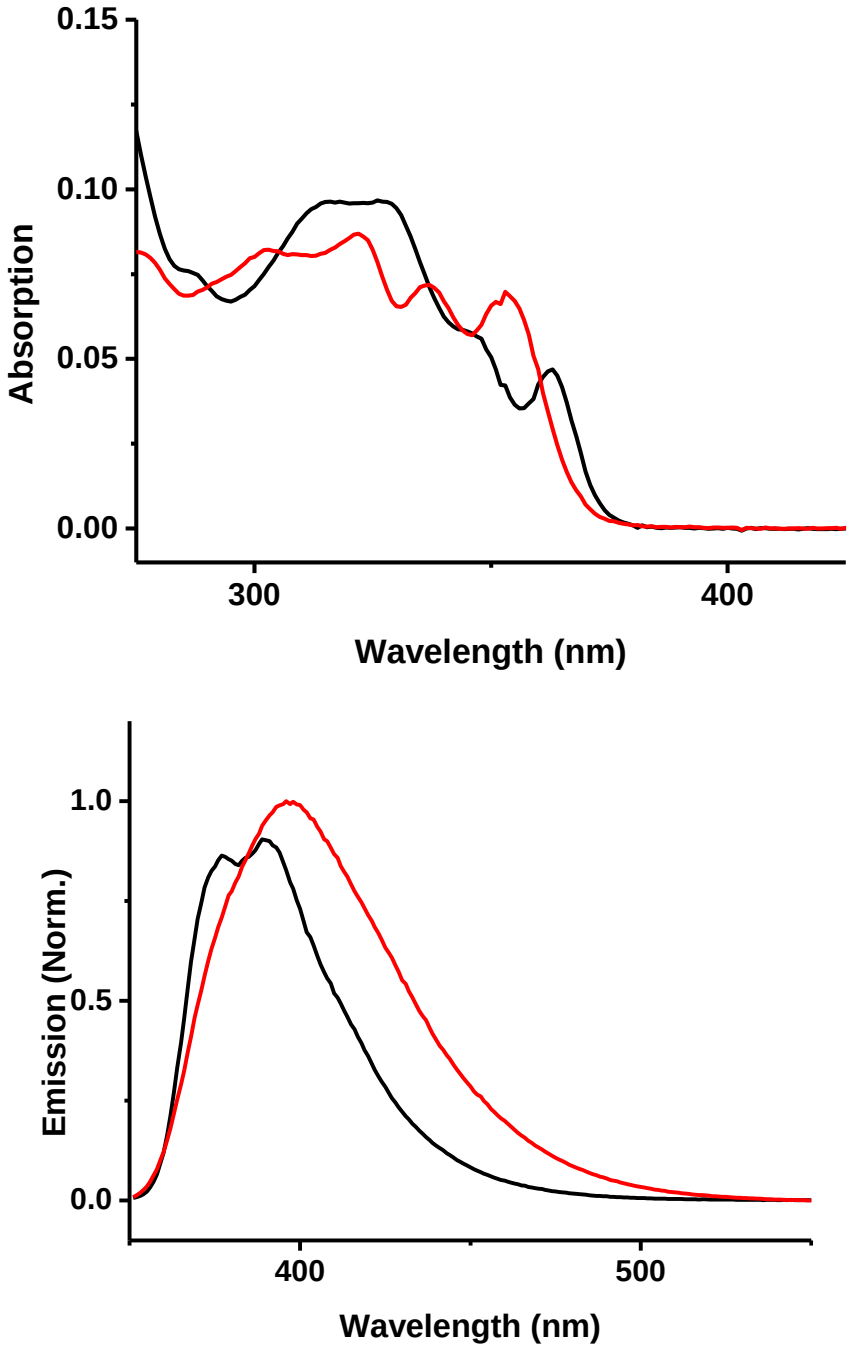


Figure S6. Absorption and fluorescence spectra of a $CHCl_3$ solution of PI-Ph (5×10^{-6} mol/L) recorded before (black) and after (red) exposure to 5.0 Gy of gamma radiation.

8. Absorption and fluorescence spectral change of PI-Ph upon HCl titration

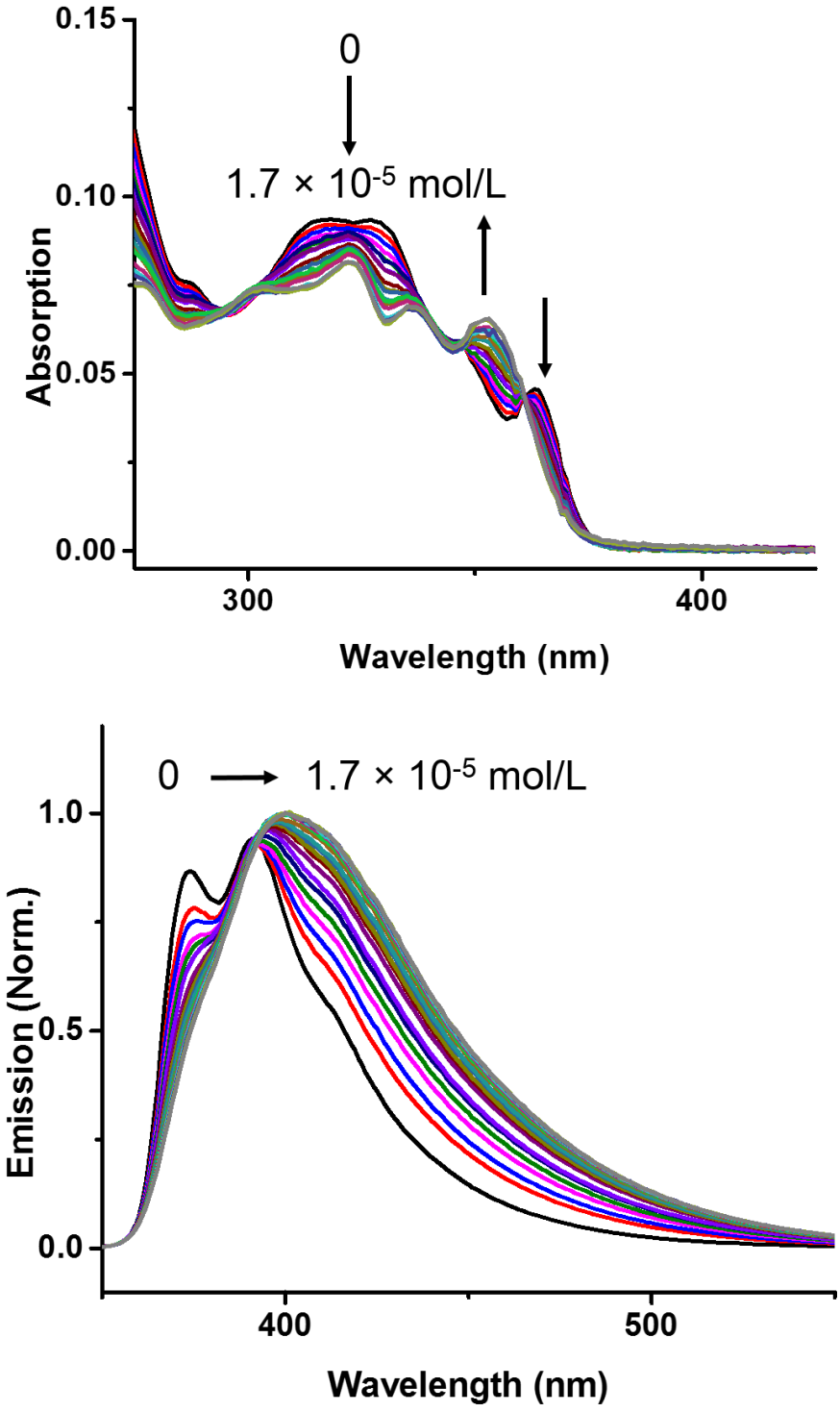


Figure S7. Absorption and fluorescence spectra of PI-Ph (5×10^{-6} mol/L $CHCl_3$ solution) upon addition in the series of concentrations of HCl.

9. Determination of binding constant of PI-Ph/HCl adduct through the HCl titration

	M	+ L	⟷ ML
Initial concentrations:	$[M]_0$	0	0
After adding [L] :	$[M]_0$-[ML]	[L]-[ML]	[ML]
Final concentrations:	0	$[L]-[M]_0$	$[M]_0$

So we have the binding constant *K*:

$$K = \frac{[ML]}{([M]_0-[ML])([L]-[ML])} \quad (2)$$

At initial state, we have the initial absorbance A_0:

$$A_0 = \varepsilon_M \cdot [M]_0 \quad (3)$$

Assuming $\varepsilon_L = 0$, after adding [L], the absorbance A will be

$$A = \varepsilon_M \cdot ([M]_0 - [ML]) + \varepsilon_{ML} \cdot [ML],$$

Rearrange this we have

$$[ML] = \frac{A-A_0}{\varepsilon_{ML}-\varepsilon_M} \quad (4)$$

At final state, we have

$$A_{final} = \varepsilon_{ML} \cdot [M]_0 \quad (5)$$

Define $\Delta\varepsilon = \varepsilon_{ML} - \varepsilon_M$, substitute (2) with (3), (4), (5), we will have

$K = \frac{\Delta\varepsilon\cdot(A-A_0)}{(\Delta\varepsilon\cdot[M]_0-A+A_0)(\Delta\varepsilon\cdot[L]-A+A_0)}$, solve *A*, then we have

$$A = \frac{1}{2\Delta\varepsilon} \cdot \left(\frac{1}{K} + [M]_0 + [L] + 2\Delta\varepsilon A_0 \pm \sqrt{\frac{1}{K^2} + \frac{2[M]_0}{K} + \frac{2[L]}{K} + [M]_0{}^2 - 2[M]_0[L] + [L]^2}\right)$$

(6)

Finally, fitting the data of Figure 4a with Eq. 6 gives K = 1.92 × 10^5 L/mol.

10. Fluorescence spectral changes of DPI-BP upon addition of other radiation decomposed products from $CHCl_3$

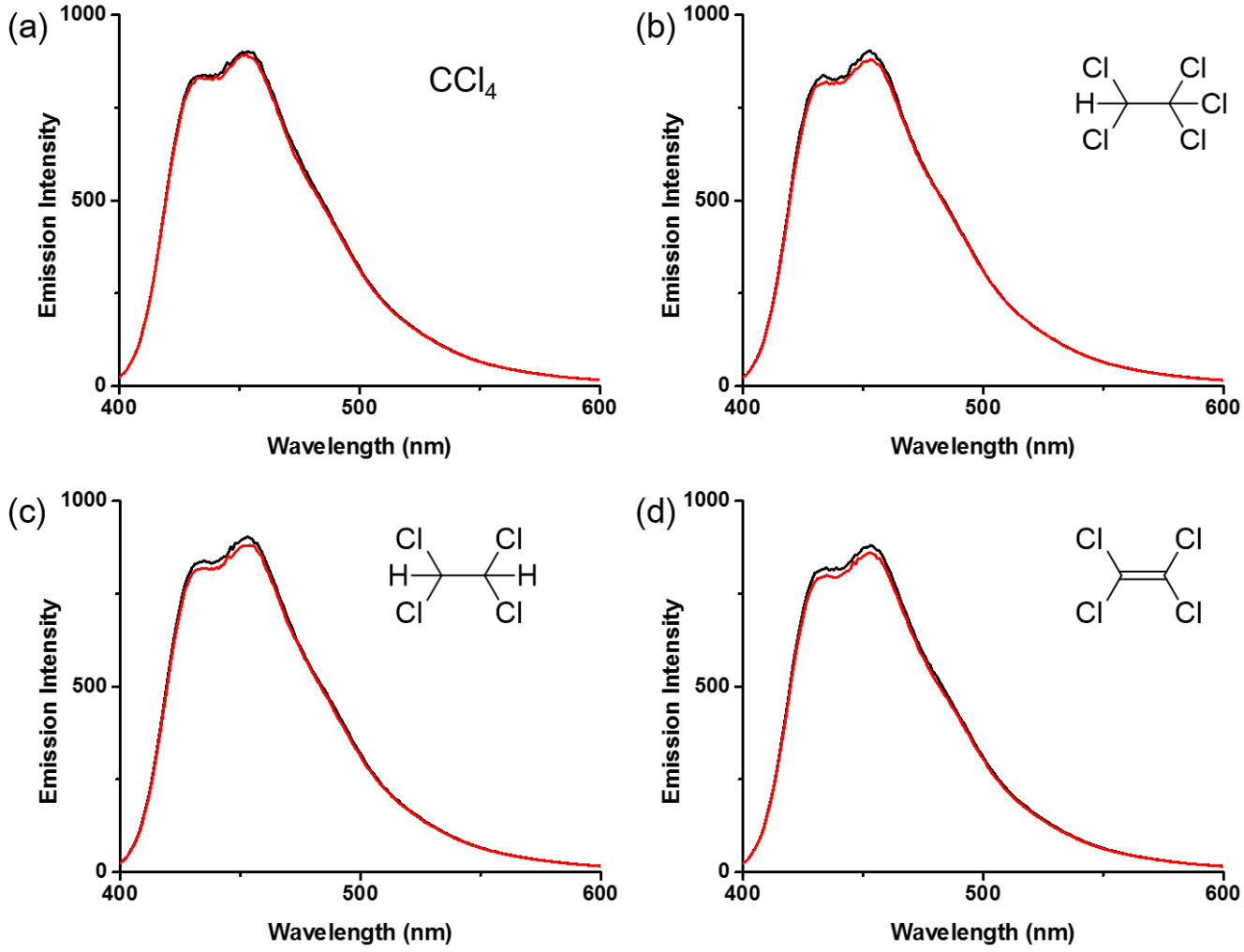


Figure S8. Fluorescence spectra of DPI-BP (5 × 10^{-6} mol/L $CHCl_3$ solution) before (black) and after (red) upon addition of 5 × 10^{-4} mol/L (a) tetrachloromethane, (b) pentachloroethane, (c) 1,1,2,2-tetrachloroethane, and (d) tetrachloroethene.

11. Fluorescence spectral reversibility test of DPI-BP

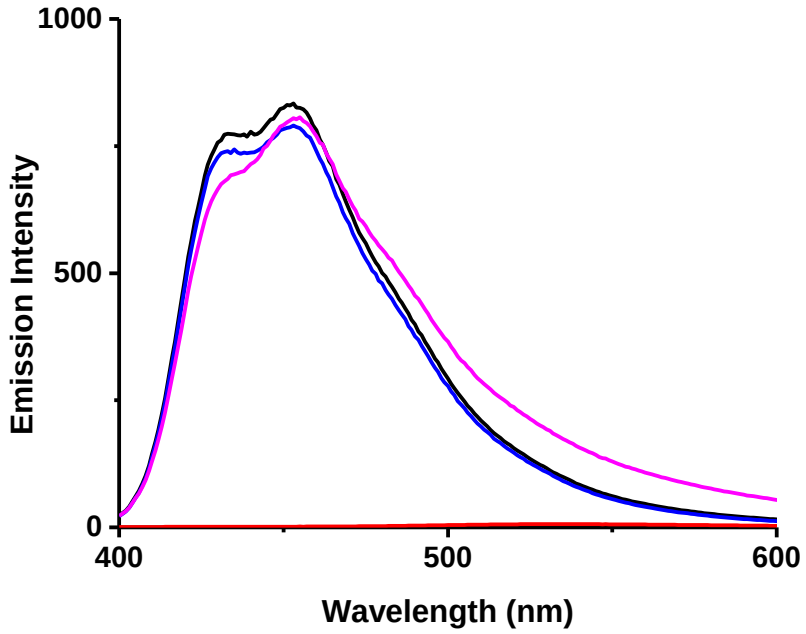


Figure S9. Fluorescence spectra of DPI-BP (5×10^{-6} mol/L $CHCl_3$ solution) before (black) and after (red, baseline) 5.0 Gy gamma radiation. The fluorescence was recovered by addition of 5×10^{-5} mol/L triethylamine (blue), or 30 μL 5×10^{-3} mol/L NaOH EtOH:H_2O = 10:1 solution, corresponding to 5×10^{-5} mol/L NaOH (purple).

12. Determination of detection limit

(a) Based on absorption measurement shown in Figure 2c

The linear domain in low dose range can be fitted as

$y = 29.495\ x - 0.619$

where y is the relative decrease in absorption ($100 \times (A_0\text{-}A)/A_0$) measured at 378 nm), and x is the gamma radiation dose.

The standard deviation (σ) is defined as $100 \times (A_{SE}/A_0)$, where A_{SE} is the standard error of the absorption measurement, as determined by the baseline measurement of blank samples (measured at 378 nm), A_0 is the absorption of DPI-BP (also measured at 378 nm). If defining three times of the standard deviation as the detectable signal, the detection limit can be projected as $3\sigma/\text{slope} = 3 \times 100 \times$

(0.00027/0.275)/29.495 = 0.01 Gy.

(b) Based on the fluorescence measurement shown in Figure 2d

The linear domain in low dose range can be fitted as

$y = 40.998\ x - 2.344$

where y is the quenching ratio percentage, x is gamma radiation dose.

The standard deviation (σ) is defined as $100 \times (I_{SE}/I_0)$, where I_{SE} is the standard error of the fluorescence intensity measurement, as determined by the baseline measurement of blank samples (monitored at 451 nm, at fixed instrumentation parameters, e.g., Ex. slit 5 nm, Em. slit 5 nm, PMT voltage 475 V), I_0 is the fluorescence intensity of DPI-BP (monitored at 451 nm, at the same instrumentation parameters). If defining three times of the standard deviation as the detectable signal, the detection limit can be projected as $3\sigma/\text{slope} = 3 \times 100 \times (0.80/898.5)/40.998 = 0.007$ Gy.