Supporting Information

A dual pyridinium-tetraarylimidazole fluorescent sensor for detection of the herbicide quizalofop-p-ethyl

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1. General and methods

All solvents and chemicals used in this work were purchased from commercial sources and used directly without further treatment. The reaction process was monitored by TLC technique. Silica gel powder (200-300 mesh) was used for column chromatography. UV-vis absorption spectra were collected on a TU-1901 UV spectrometer. Fluorescence emission spectra were obtained on a FS5 fluorescence spectrometer (Ediburgh Instruments, UK). The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker ARX400 nuclear magnetic resonance spectrometer at 400 MHz and 100 MHz, respectively. Mass spectra were measured on a Bruker Microflex type mass spectrometer. Theoretical calculations were performed using a density-functional theory (DFT) approach at the B3LYP/6-31G (d) level of the Gaussian 09 program. The absolute fluorescence yields (ΦF) were evaluated on an Edinburgh Instruments FLS920 Fluorescence Spectrometer with a 6-inch integrating sphere. Compounds **1** and **2** were prepared according to the published procedures (1. Gao, T.; Yang, S.; Cao, X.; Dong, J.; Zhao, N.; Ge, P.; Zeng, W.; Cheng, Z., Smart Self-Assembled Organic Nanoprobe for Protein-Specific Detection: Design, Synthesis, Application, and Mechanism Studies. Anal. Chem. 2017, 89 (18), 10085-10093; 2. Kassab RM, Khalil FSAM, Abbas AA. Synthesis and Antimicrobial Activities of Some New Bis(Schiff Bases) and Their Triazole-Based Lariat Macrocycles. Polycyc Aromatic Compounds. 2020;42(5):2751-66).

1 Spectral analysis procedure

Under stirring at room temperature, **DPT** was dissolved in DMSO-H_2O (5:95) to prepare a stock solution at a concentration of 0.1 mM. Analytes were dissolved in DMSO-H_2O (5:95) to obtain the corresponding concentration (these concentrations were ten times the final test concentrations). Subsequently, 1.0 mL of prepared **DPT** solution and 1.0 mL of prepared analytes solution were mixed and diluted to 10 mL with DMSO-H_2O (5:95), which were further examined by fluorescence spectra and UV-Vis spectra.

2 Preparation of pH solution

The ultrapure water, DMSO, NaOH, and HCl were used to prepare DMSO-H_2O (5:95) solution in corresponding pH values, which was further used for experiments of pH influence on sensing quizalofop-p-ethyl. The pH values were determined by a Mettler-Toledo pH meter.

3 The experimental procedure of detecting quizalofop-p-ethyl in test paper, soil and plastic film

Pieces of neutral filter paper were immersed in DMSO-H_2O (5:95) solution of **DPT** (0.1 mM) for 1 minute. After drying at room temperature, these papers were cut into a circular shape. Then these circular papers were immersed in the DMSO-H_2O (5:95) solution of various guests (0.1 mM) for 30 s. Subsequently, after drying in air again, the fluorescence of these papers was observed under UV_{365nm} light to obtain the fluorescence photographs. On the other hand, these circular papers were immersed in the DMSO-H_2O (5:95) solution of quizalofop-p-ethyl in different concentrations (0.0 mM, 0.2 mM, 0.4 mM, 0.6 mM, 0.8 mM, and 1.0 mM) for 30 s. Subsequently, after drying in air again, the fluorescence of these papers was observed under UV_{365nm} light to obtain the fluorescence photographs.

In addition, DMSO-H_2O (5:95) solution of quizalofop-p-ethyl (0.1 mM) was sprayed on the soil or written on the plastic film with word of “happy”. After drying in air for 24 hours, the DMSO-H_2O (5:95) solution of **DPT** (0.1 mM) was sprayed on soil or plastic film again. After 5 minutes, the soil and plastic films were observed under UV_{365nm} light to obtain the fluorescence photographs.

4 The experimental procedure of analyzing stimulated water samples

The certain amount of quizalofop-p-ethyl was added in the solution of DMSO-H_2O (5:95) (tap water or water of Minjiang river) to prepare quizalofop-p-ethyl solution in 1.0×10^{-5} M, 2.0×10^{-5} M and 3.0×10^{-5} M, respectively. On the other hand, 1.0×10^{-4} M of **DPT** solution was prepared in DMSO-H_2O (5:95) with tap water and water of Minjiang river, respectively. Then, 1.0 mL of prepared quizalofop-p-ethyl solution in corresponding concentration was mixed with 1.0 mL of prepared **DPT** solution, following that the mixture was diluted to 10 mL by DMSO-H_2O (5:95) (tap water or water of Minjiang river). As a result, the concentration of **DPT** was 1.0×10^{-5} M, and the concentrations of oxyfluorfen were 1.0×10^{-6} M, 2.0×10^{-6} M and 3.0×10^{-6} M in these solutions,

respectively. The obtained solutions were then examined by fluorescence spectra to evaluate the fluorescence intensity (λ_{ex} = 400 nm), which was further compared by the standard working curve (the equation in the inserted scheme in Figure 3b: Y = 4842.05X + 578.22). The values of X were then obtained and filled as found concentration in Table 1. All data were performed by three independent experiments and the STDs were then calculated. The calculation is based on the sample standard deviation formula:

$$S = \sqrt{\frac{\Sigma_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}$$

where x_i is the recovery from an individual replicate and x_i is the mean recovery from all n replicates.

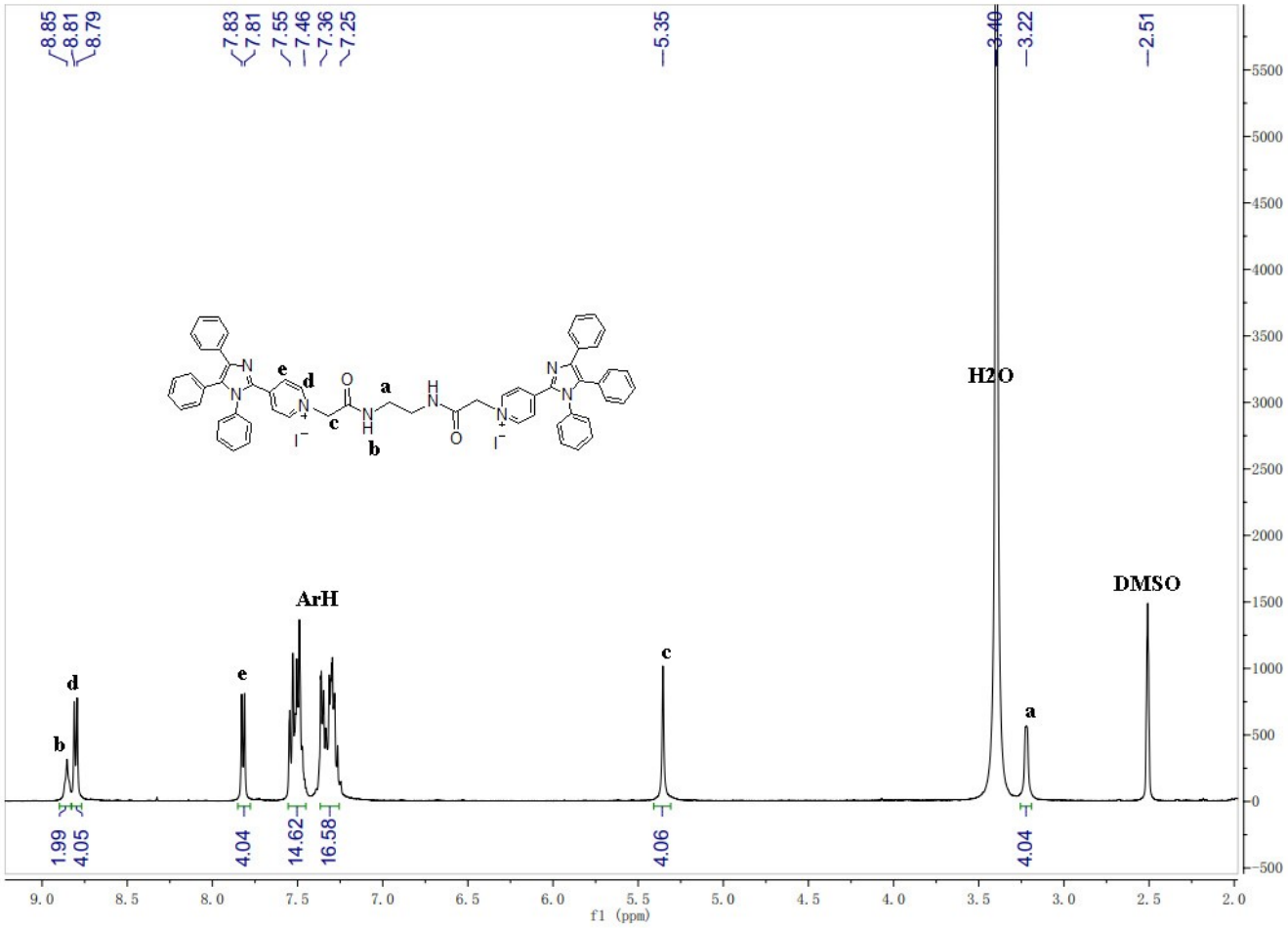


Figure S1 The ^{1}H NMR spectrum of **DPT** in DMSO-d_6.

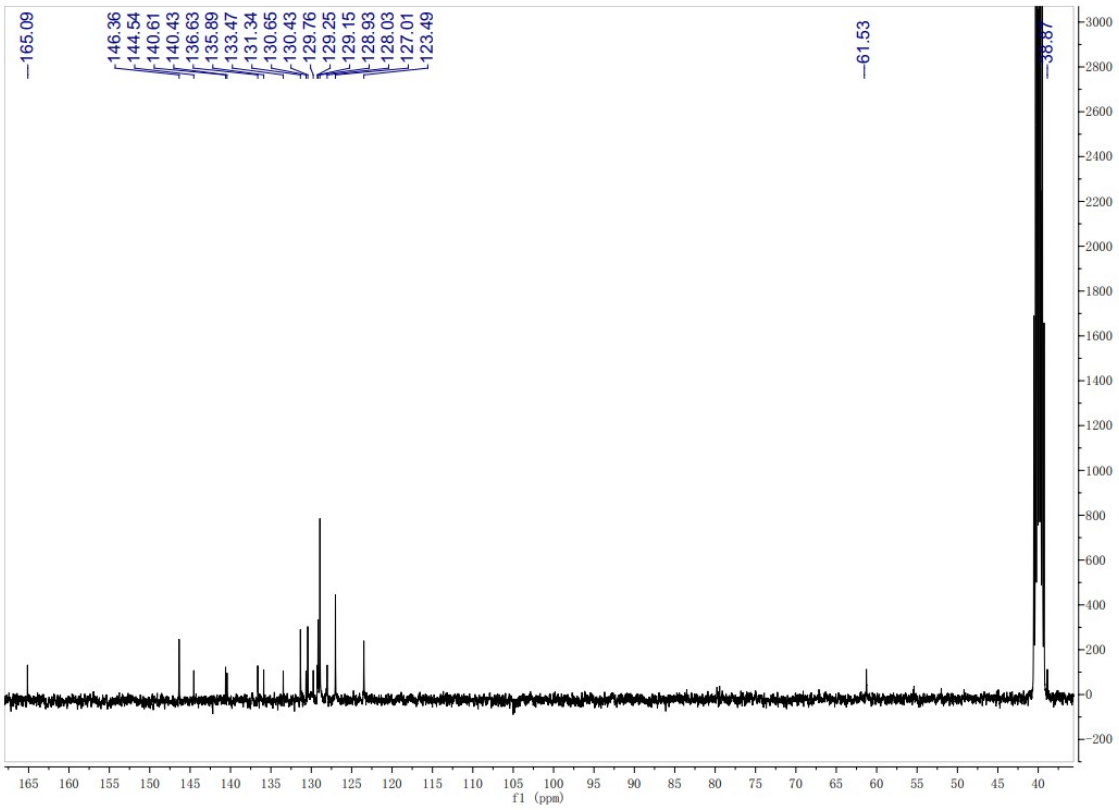


Figure S2 The ^{13}C NMR spectrum of **DPT** in DMSO-d_6.

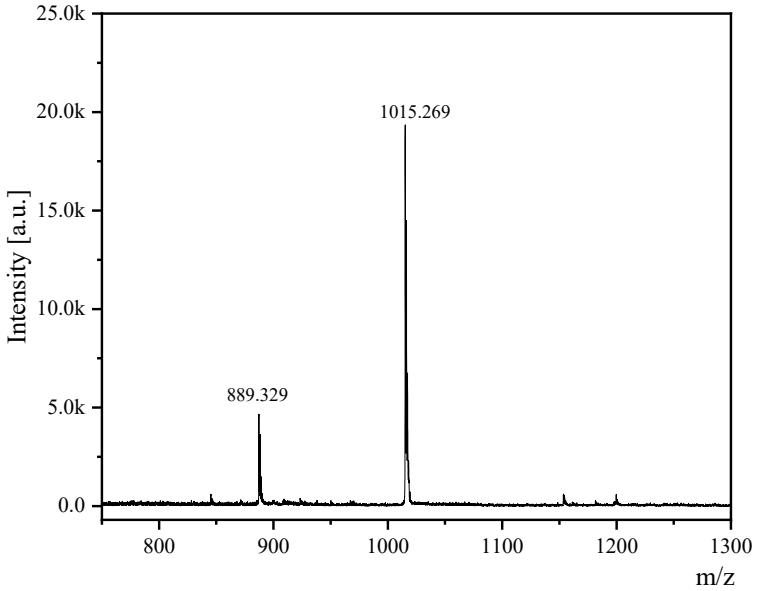


Figure S3 MALDI-TOF-MS spectrum of **DPT**

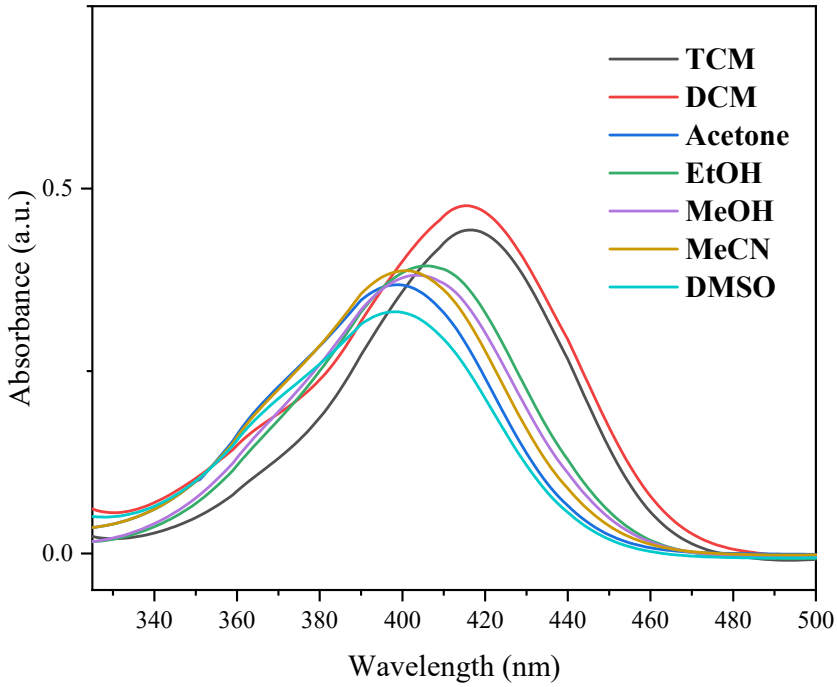


Figure S4 UV-vis absorption spectra of **DPT** in different solvents (1.0×10^{-5} M)

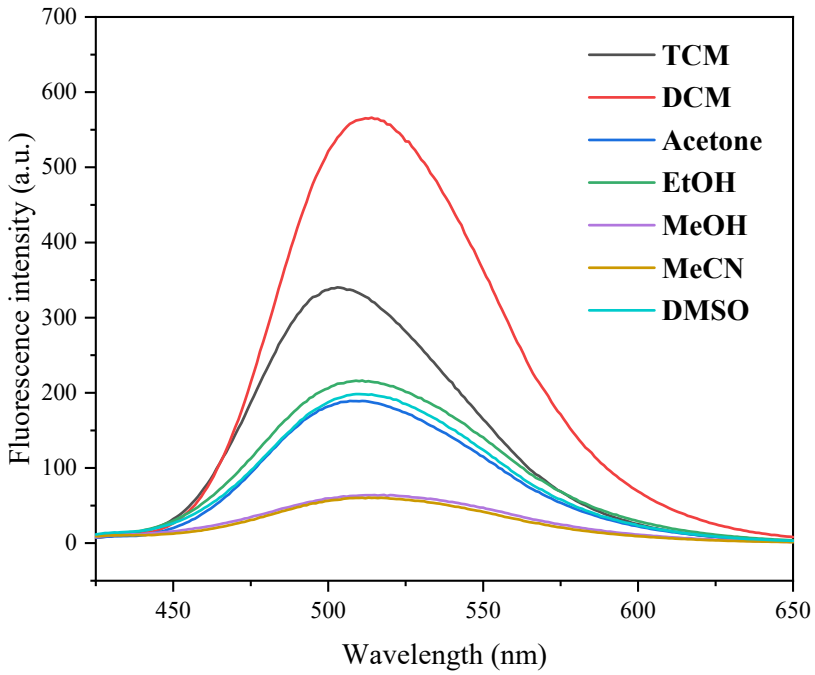


Figure S5 Fluorescence emission spectra of **DPT** in different solvents (1.0×10^{-5} M, λ_{ex}= 400 nm)

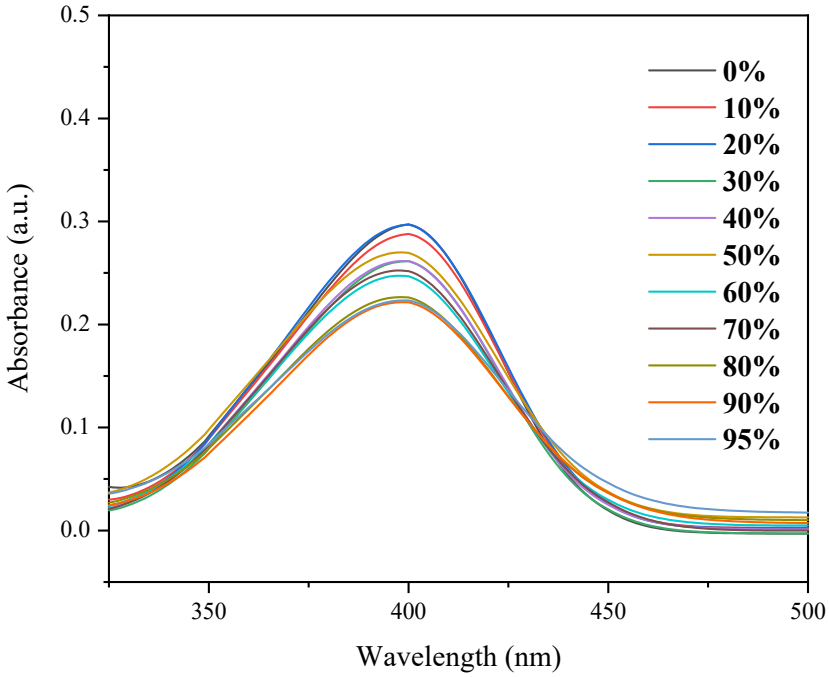
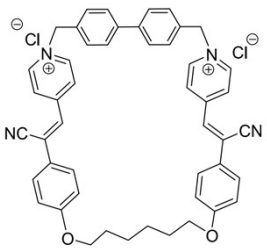
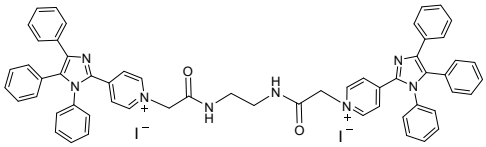


Figure S6 UV-vis absorption spectra of **DPT** in DMSO-H_2O with different water contents (1.0×10^{-5} M)

Table S1 Comparison of DL for sensing quizalofop-p-ethyl

Method	LOD	Reference
GC-MS	2.68×10^{-7} M	J Food Compost Anal. 2023;115.
LC-MS	6.70×10^{-6} M	Environ Monit Assess. 2023;195(9):1067.
UHPLC-Orbitrap-MS	1.44×10^{-11} M	Ecotoxicol Environ Saf. 2018;157:285-91.
HPLC-MS	2.0×10^{-8} M	Foods. 2022;11(7).
Gold nanoparticle-based lateral flow immunoassay	2.68×10^{-8} M	Sci Total Environ. 2023;857(Pt 1):159427.
Fluorescence measurement of eosin Y in the presence of Pd(II)	5.45×10^{-8} M	Spectrochim Acta A Mol Biomol Spectrosc. 2017;174:301-6.
	2.98×10^{-8} M	Talanta. 2024;276:126269.
	1.05×10^{-7} M	this work

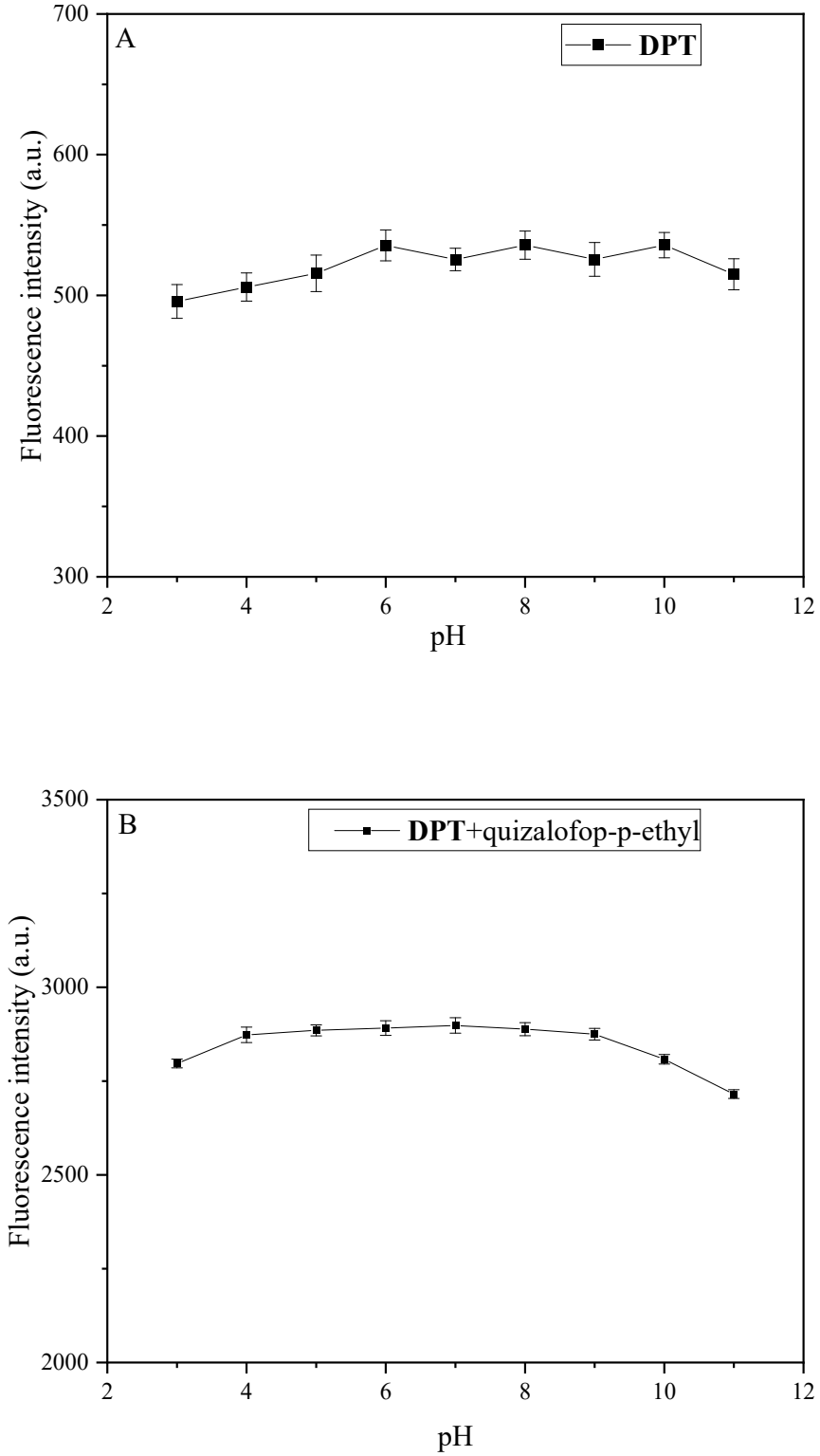


Figure S7 (A) The influence of pH on the maximum fluorescence intensities of **DPT** (λ_{ex} = 400 nm, 1.0×10^{-5} M in DMSO-H_2O (5:95) solution) and **DPT** + quizalofop-p-ethyl**.** (λ_{ex} = 400 nm, 1.0×10^{-5} M each in DMSO-H_2O (5:95) solution)

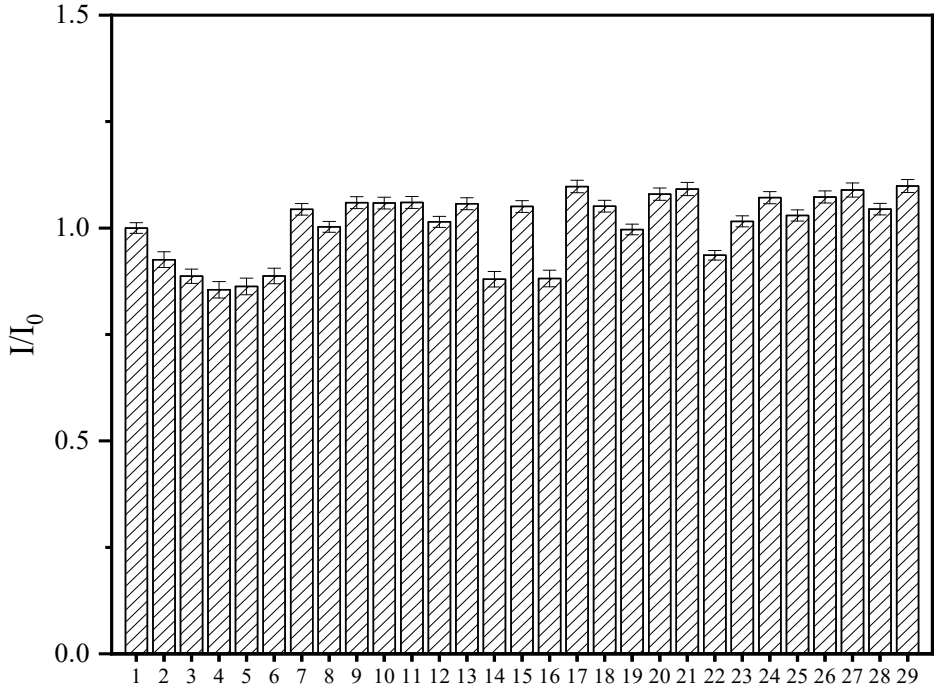


Figure S8 The interference experiments of **DPT** (1.0×10^{-5} M) with quizalofop-p-ethyl in prescence of the interfering species (1×10^{-5} M each, λ_{ex} = 400 nm) in DMSO-H_2O (5:95) solution. I_0 was the fluorescence intensity of **DPT** with quizalofop-p-ethyl and I was the fluorescence intensity of **DPT** with quizalofop-p-ethyl in prescence of the interfering species. 1 = **DPT** + quizalofop-p-ethyl, 2 = 1 + pymetrozine, 3 = 1 + imidacloprid, 4 = 1 + glufosinate-ammonium, 5 = 1 + glyphosate isopropylamine salt, 6 = 1 + mancozeb, 7 = 1 + hymexazol, 8 = 1 + thiophanate-methyl, 9 = 1 + ulfometuron-methyl, 10 = 1+ bromoxynil octanoate, 11 = 1 + monosultap, 12 = 1 + niclosamide ethanolamine salt, 13 = 1 + metaldehyde, 14 = 1 + tricyclazole, 15 = 1 + cartap hydrochloride, 16 = 1 + Na^+, 17 = 1 + K^+, 18 = 1 + Al^{3+}, 19 = 1 + Ba^{2+}, 20 = 1 + Ca^{2+}, 21 = 1 + Mg^{2+}, 22 = 1 + Cu^{2+}, 23 = 1 + Zn^{2+}, 24 = 1 + NH_4^+, 25 = 1 + SO_4^{2-}, 26 = 1 + Cl^-, 27 = PO_4^{3-}, 28 = NO_3^-, 29 = HPO_4^{2-}.

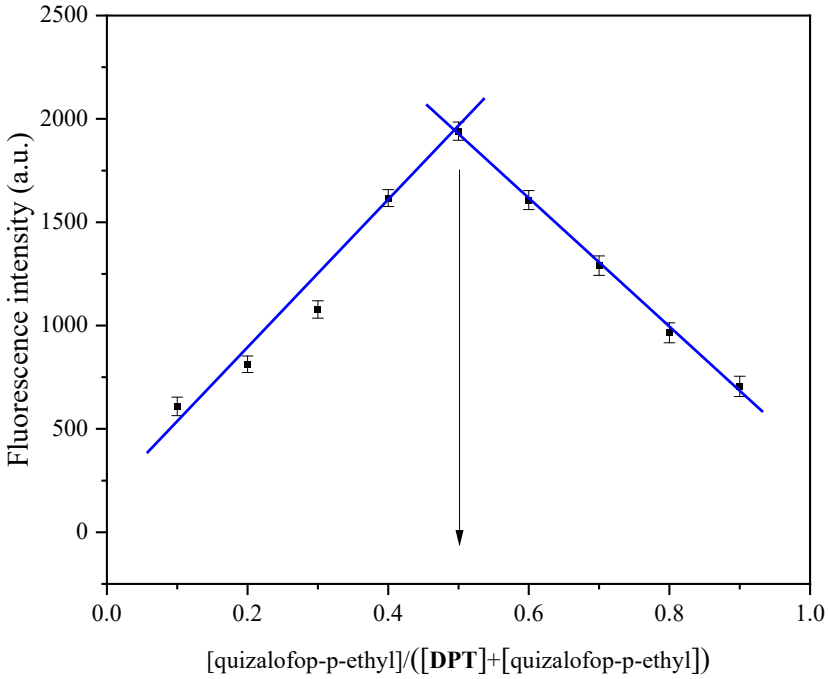


Figure S9 Job's plot for **DPT** + quizalofop-p-ethyl (λ_{ex} = 400 nm) in DMSO-H_2O (5:95) solution (The total concentration was 1.0×10^{-5} M).

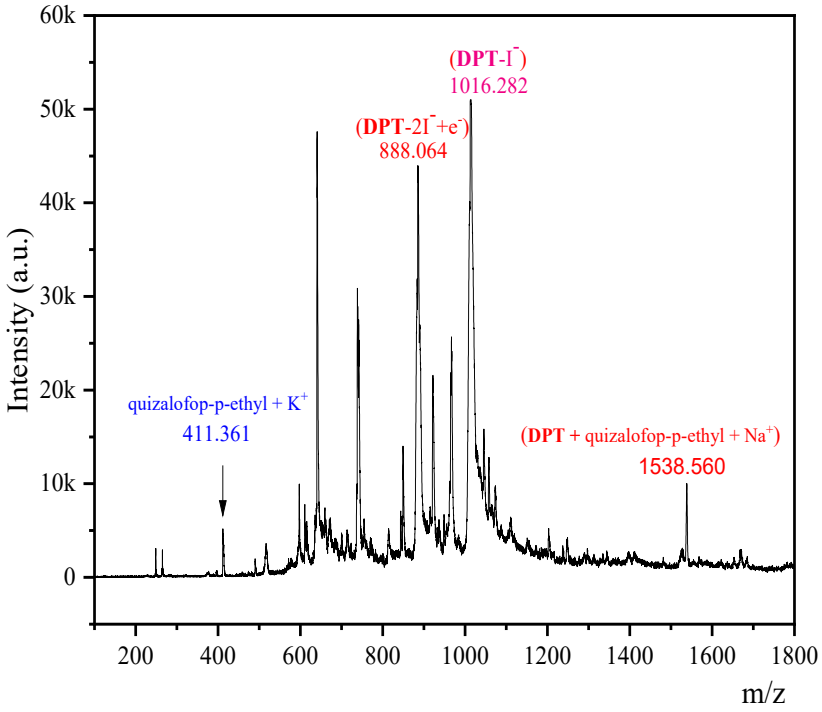


Figure S10 The binding MS spectrum for **DPT** with quizalofop-p-ethyl (1:1) in DMSO-d_6.

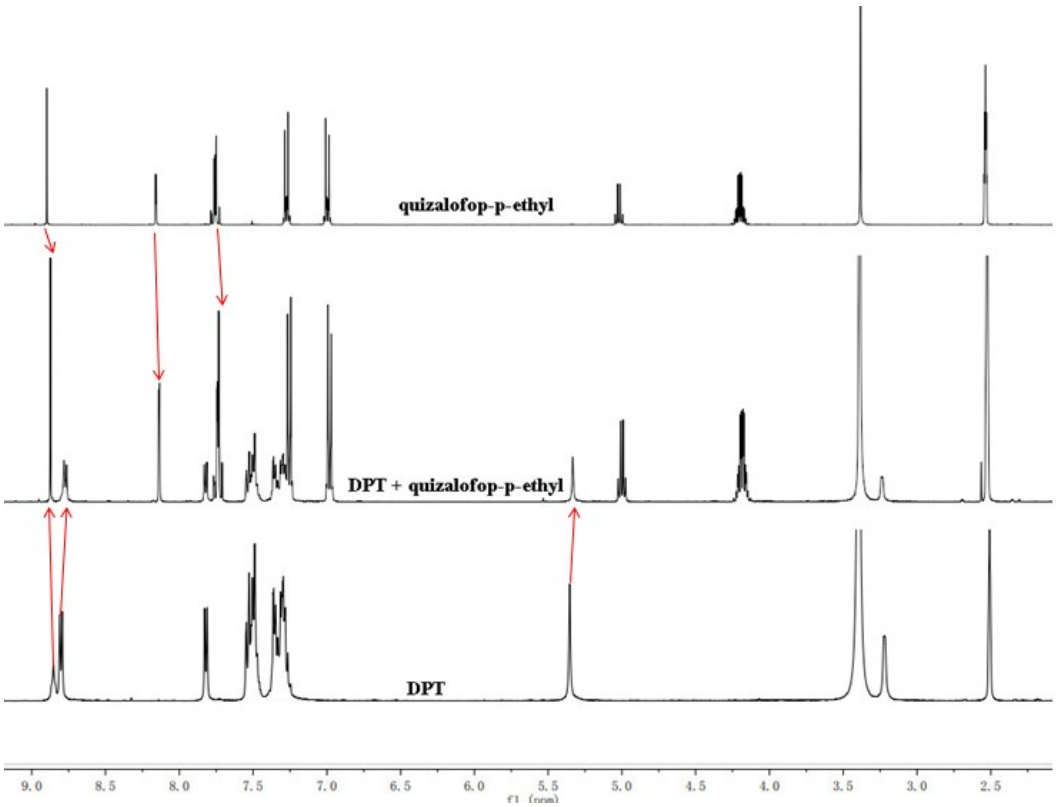


Figure S11 The comparison of ^{1}H NMR spectra of **DPT** with quizalofop-p-ethyl (1:1) in DMSO-d_6.

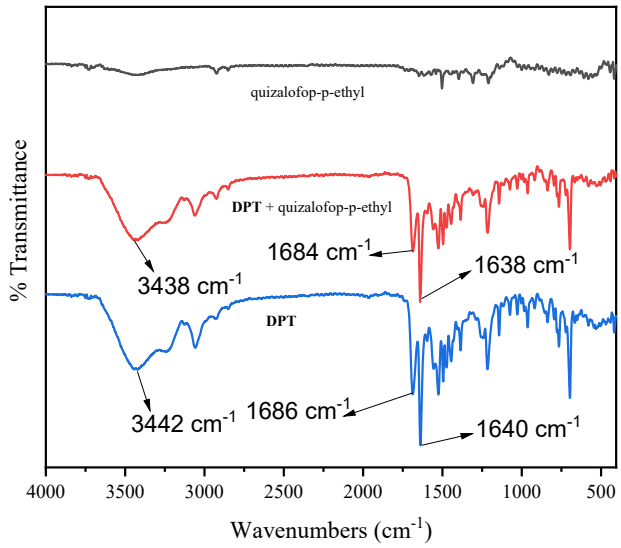


Figure S12 The comparison of FT-IR spectra of **DPT**, quizalofop-p-ethyl and **DPT** with quizalofop-p-ethyl (1:1)

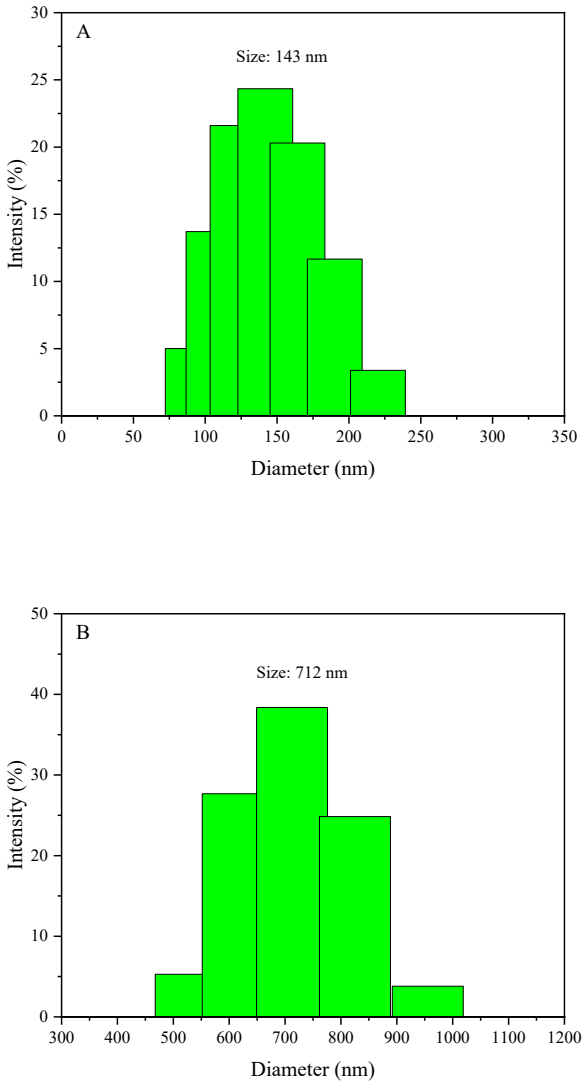


Figure S13 Particle size analysis of (A) **DPT** in DMSO-H_2O (5:95); and (B) **DPT** with quizalofop-p-ethyl in DMSO-H_2O (5:95)

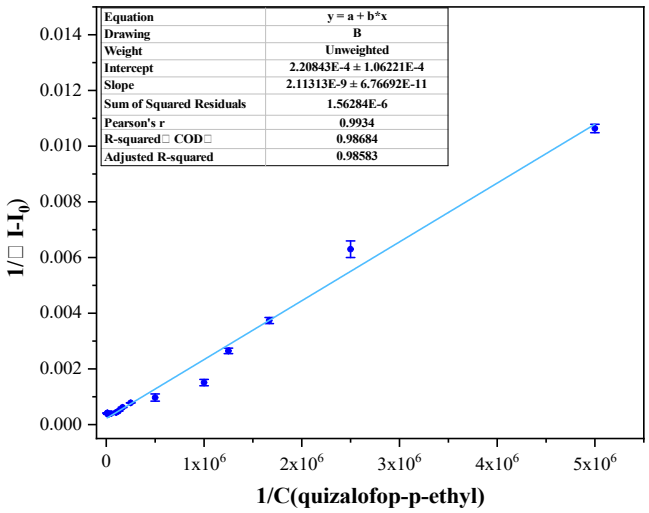


Figure S14 The calulation of binding constants (Ka) based on fluorescence titration by Benesi-Hildebrand equation.

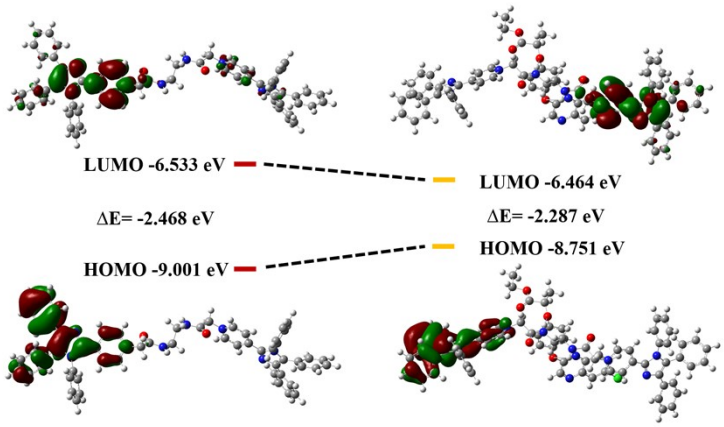


Figure S15 HOMO-LUMO energy levels of **DPT** before and after binding quizalofop-p-ethyl

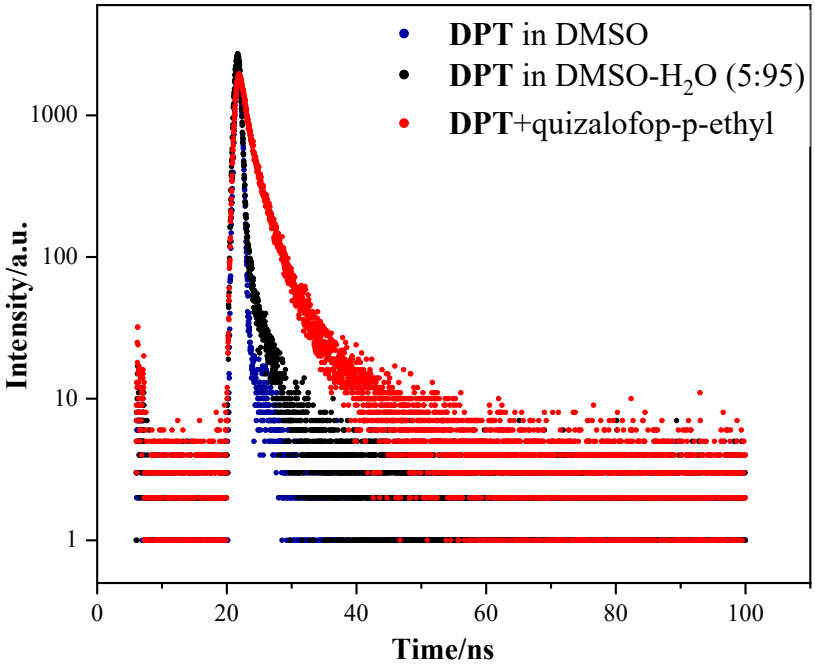


Figure S16 The fluorescence lifetime spectra of **DPT** (Black & Blue) and **DPT** with quizalofop-p-ethyl (Red)

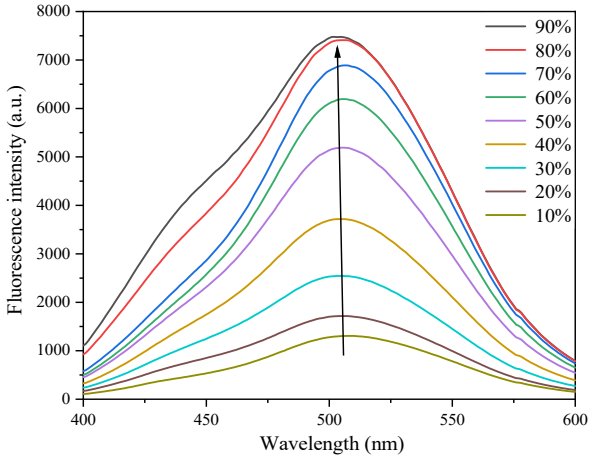


Figure S17 Fluorescence emission of **DPT** in DMSO-glycerol solution with different glycerol contents (1.0×10^{-5} M, $\lambda_{ex} = 400$ nm)