

Supporting Information

Amide-substituted cyanostilbene-pyridine macrocycle: A "turn-on" fluorescent sensor for herbicide quizalofop-p-ethyl

Pan He^{a,b,c}, Xinyu Fang^a, Liangbin Lin^{*a}, Hongyu Guo^{*a,b}, and Fafu Yang^{*a,c}

^a*College of Chemistry and Materials Science, Fujian Normal University, Fuzhou 350007, P. R. China; Email: yangfafu@fjnu.edu.cn.*

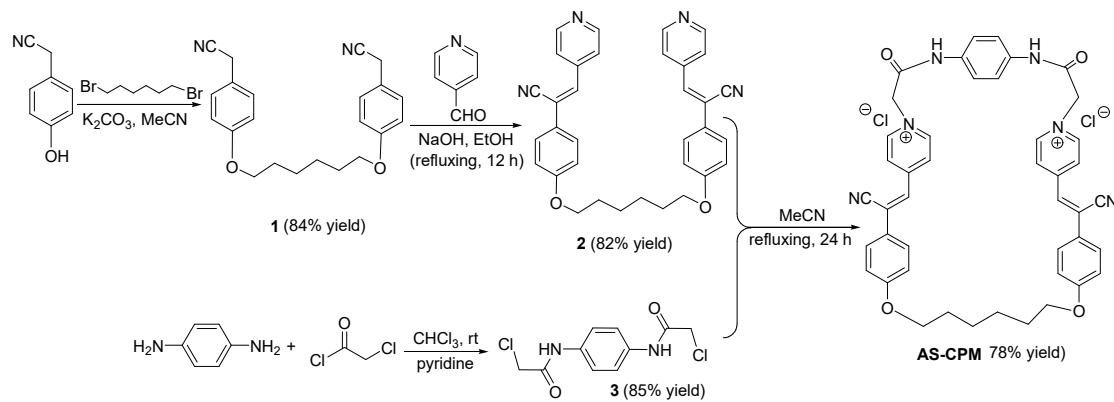
^b*Fujian Key Laboratory of Polymer Materials, Fuzhou 350007, P. R. China.*

^c*Fujian provincial Key Laboratory of Advanced Materials Oriented Chemical Engineering, Fuzhou 350007, P. R. China.*

1. General and methods

The solvents and chemicals were purchased from commercial sources and treated by standard procedures before use. The reaction process was monitored by TLC technique. Silica gel powder (200-300 mesh) was employed for the rapid column chromatography. UV-vis absorption spectra were examined by TU-1901 UV spectrometer. Fluorescence spectra were tested on FS5 fluorescence spectrometer (Edinburgh Instruments, UK). The ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were collected on Bruker ARX400 nuclear magnetic resonance spectrometer. Mass spectra were explored on Bruker mass spectrometer. The absolute fluorescence yields (Φ_F) were obtained on Edinburgh Instrument FLS920 Fluorescence Spectrometer with a 6-inch integrating sphere. Compounds **1** and **2** were prepared according to the published procedure (He P, Chen Y, Lin L, Guo H, Yang F. A "turn-on" fluorescent sensor for herbicide quizalofop-p-ethyl based on cyanostilbene-

pyridine macrocycle. *Talanta* 2024, 276, 126269). Compound **3** was obtained by the reported method (Wang L, Zhang Y, Ding L, Liu J, Zhao B, Deng Q, Yan T. Synthesis and physiochemical properties of novel gemini surfactants with phenyl-1,4-bis(carbamoylmethyl) spacer. *Royal Society of Chemistry Advances* 2015, 5, 74764-74773).



Scheme S1 Synthesis route of **AS-CPM**

2. Spectral analysis procedure

A stock solution of 0.1 mM was prepared by dissolving **AS-CPM** in DMSO-H₂O (5:95) under stirring at room temperature. The 0.1 mM stock solution of analyte was also prepared in DMSO-H₂O (5:95). Subsequently, 0.1 mL of prepared **AS-CPM** solution and 0.1 mL of prepared analyte solution were mixed and diluted to 10 mL with DMSO-H₂O (5:95) for further detection by fluorescence spectroscopy and UV-Vis spectroscopy.

3. Preparation of pH solution

The ultrapure water, DMSO, NaOH and HCl were used to prepare DMSO-H₂O (5:95)

solution in corresponding pH values, which was further used for experiments of pH influence on sensing halosulfuron-methyl. The pH values were examined by Mettler-Toledo pH meter.

4. The experimental procedure of detecting quizalofop-p-ethyl in test paper and agricultural products.

Three drops of DMSO-H₂O (5:95) solution of **AS-CPM** (0.1 mM) were added on the circular neutral test papers. After drying at room temperature, three drops of various guests (0.1 mM) in DMSO-H₂O (5:95) solution were added again on these circular test papers. After drying in air, they were placed under UV_{365 nm} lamp for observation and corresponding fluorescent photographs were obtained. On the other hand, different concentrations (0.0 mM, 0.02 mM, 0.04 mM, 0.06 mM, 0.08 mM and 0.1 mM) of quizalofop-p-ethyl DMSO-H₂O (5:95) solution were uniformly added to the test paper, dried in the air and then placed under UV_{365 nm} lamp to obtain the corresponding fluorescence photographs.

On the other hand, a DMSO-H₂O (5:95) solution of quizalofop-p-ethyl (0.1 mM) was sprayed on tomatoes, tangerine and eggplants. After drying naturally in air, DMSO-H₂O (5:95) solution of **AS-CPM** (0.1 mM) was added dropwise to these products. The fluorescence of these products was then observed under UV_{365 nm} lamp and the corresponding fluorescence photographs were obtained. DMSO-H₂O (5:95) solution of quizalofop-p-ethyl (0.1 mM) and DMSO-H₂O (5:95) solution of **AS-CPM** (0.1 mM) were sprayed on loquat leaf separately, and the fluorescence photographs were observed under UV_{365nm} light and taken. Further, DMSO-H₂O (5:95) solution of

quizalofop-p-ethyl (0.1 mM) was sprayed on loquat leaf, followed by DMSO-H₂O (5:95) solution of AS-CPM (0.1 mM), and fluorescence photographs were taken under UV _{365nm} light.

5. The experimental procedure of analyzing real water samples

The certain amount of quizalofop-p-ethyl was added in the solution of DMSO-H₂O (5:95) (tap water or water of Minjiang river) to prepare the quizalofop-p-ethyl solution in 2.0×10^{-6} M, 4.0×10^{-6} M and 6.0×10^{-6} M, respectively. On the other hand, 1.0×10^{-5} M of **AS-CPM** solution was prepared in DMSO-H₂O (5:95) solution 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 **CPM** solution, following that the mixture was diluted to 10 mL by DMSO-H₂O (5:95) (tap water or water of Minjiang river). As a result, the concentration of **AS-CPM** was 1.0×10^{-6} M, and the concentrations of halosulfuron-methyl were 0.2×10^{-6} M, 0.4×10^{-6} M and 0.6×10^{-6} M in these solutions, respectively. The obtained solutions were then examined by fluorescence spectra to evaluate the fluorescence intensity ($\lambda_{ex} = 390$ nm), which was further compared by the standard working curve (the equation in the inserted scheme in Figure 2B: $Y = 91.6081 + 4467.9574X$). 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 RSD were then calculated.

6. Synthesis of Probe AS-CPM

The mixture of compound **2** (0.579 g, 1.1 mmol), compound **3** (0.287 g, 1.1 mmol) and KI (0.183 g, 1.1 mmol) were stirred and refluxed in 30 mL of anhydrous acetonitrile for 24 h. As the materials were reacted out, the solvent was removed by reduced pressure. The residue was rinsed fully by 30 mL of dichloromethane and 30 mL of anhydrous ethanol in sequence. The obtained solid was recrystallized in 20 mL of DMSO-hexane (1:1). **AS-CPM** was collected as a red solid in yield of 78%. ¹H NMR (400 MHz, DMSO-d6) δ : 10.84 (bs, 2H, NH), 9.10 (d, J = 4.0 Hz, 4H, C₅H₄N), 8.49 (d, J = 4.0 Hz, 4H, C₅H₄N), 8.26 (s, 2H, CH=CCN), 7.87 (d, J = 8.0 Hz, 4H, ArH), 7.60 (s, 4H, ArH), 7.19 (d, J = 8.0 Hz, 4H, ArH), 5.66 (bs, 4H, NCH₂CO), 4.11 (bs, 4H, OCH₂), 1.80 (bs, 4H, CH₂), 1.53 (bs, 4H, CH₂). ¹³C NMR (100 MHz, DMSO-d6) δ : 161.72, 150.17, 145.54, 140.66, 134.09, 130.16, 129.06, 128.11, 127.39, 124.91, 119.89, 116.80, 115.92, 68.47, 62.98, 29.15, 25.82. MALDI-TOF-MS (C₄₄H₄₀N₆O₄Cl₂) Calcd. For m/z = 716.311 [M-2Cl⁻+e⁻]⁺, found: 716.806 [M-2Cl⁻+e⁻]⁺. Anal. calcd for C₄₄H₄₀N₆O₄Cl₂: C 67.09, H 5.12, N 10.67; Found: C 67.05, H 5.15, N 10.60.

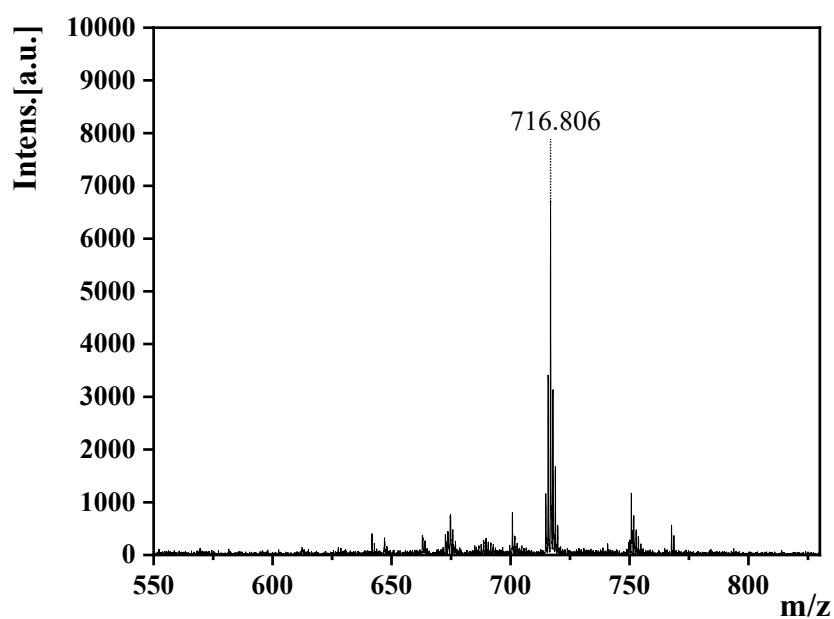


Figure S1 MALDI-TOF-MS spectrum of AS-CPM

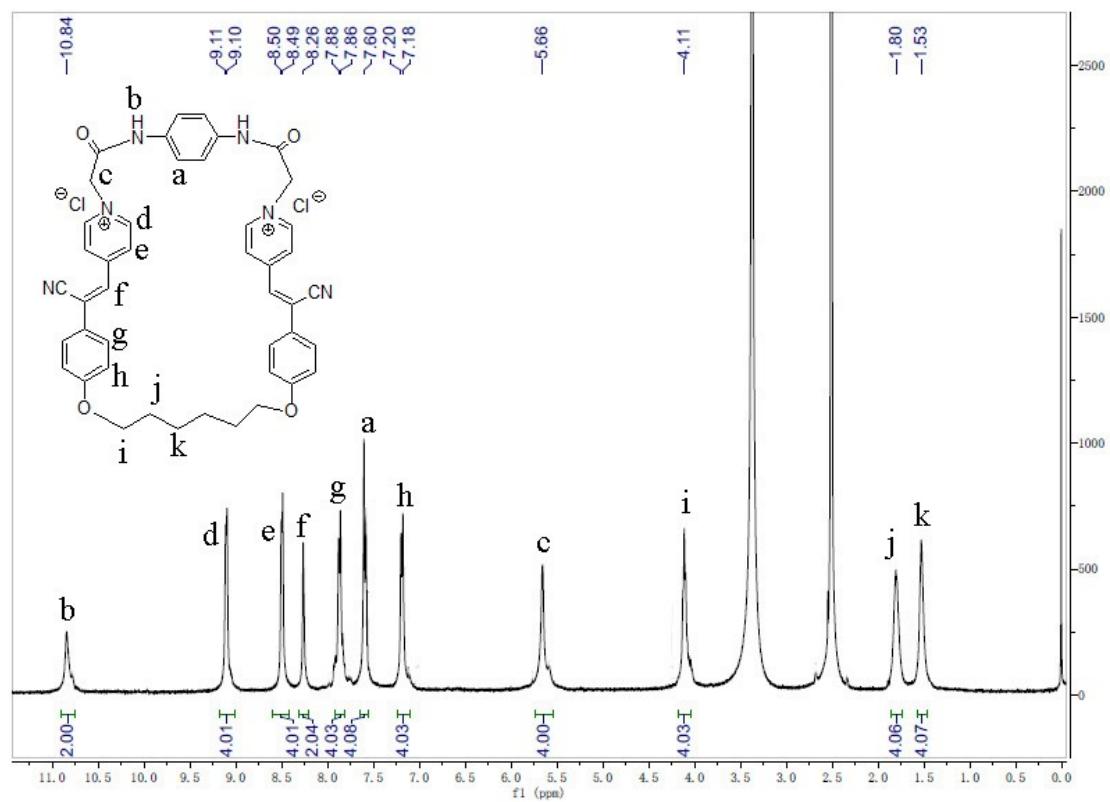


Figure S2 The ¹H NMR spectrum of AS-CPM

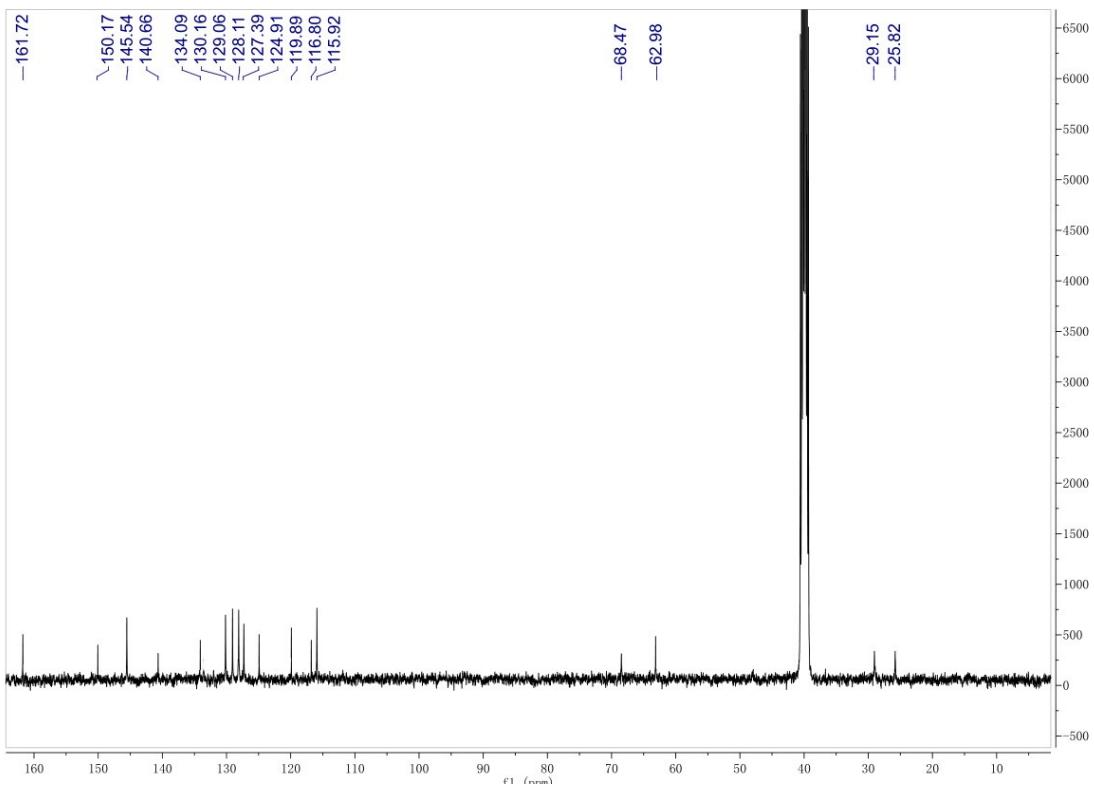


Figure S3 The ^{13}C NMR spectrum of AS-CPM

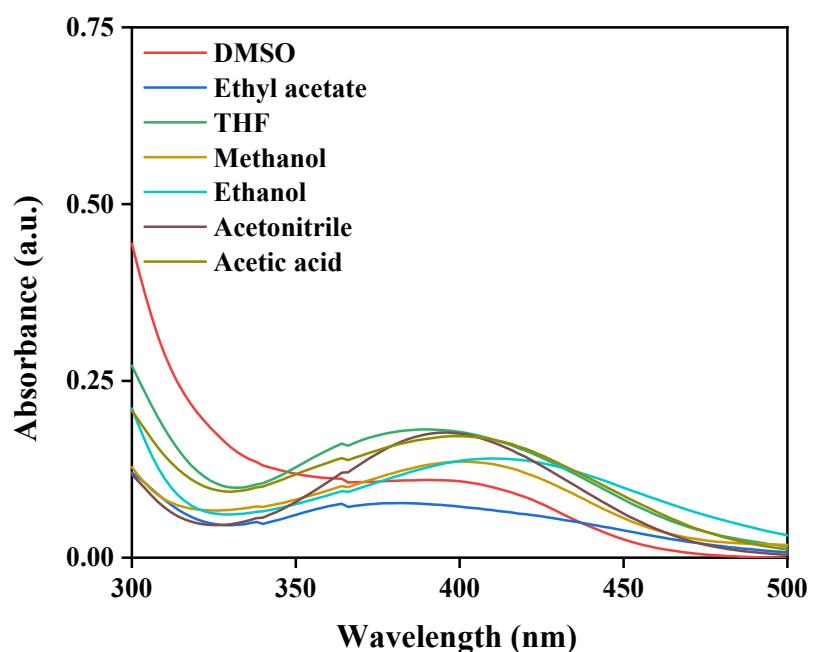


Figure S4 UV-vis absorption spectra of AS-CPM in different solvents (1.0×10^{-6} M)

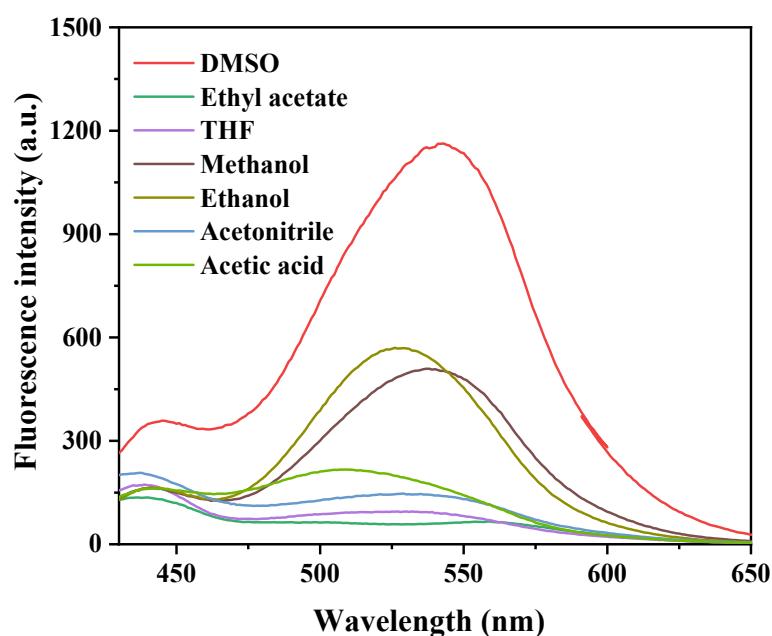


Figure S5 Fluorescence spectra of AS-CPM (1 μ M) in different solvents

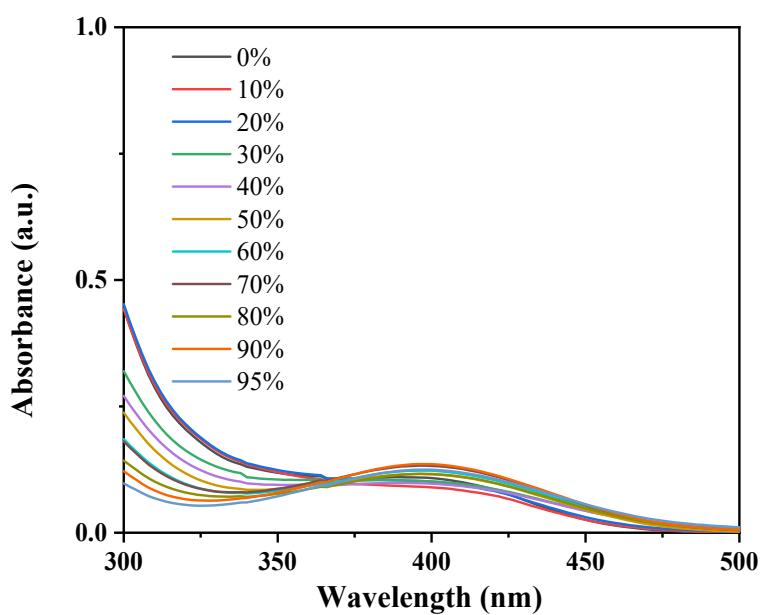


Figure S6 UV spectra of AS-CPM in DMSO-H₂O with different water contents (1.0 μ M)

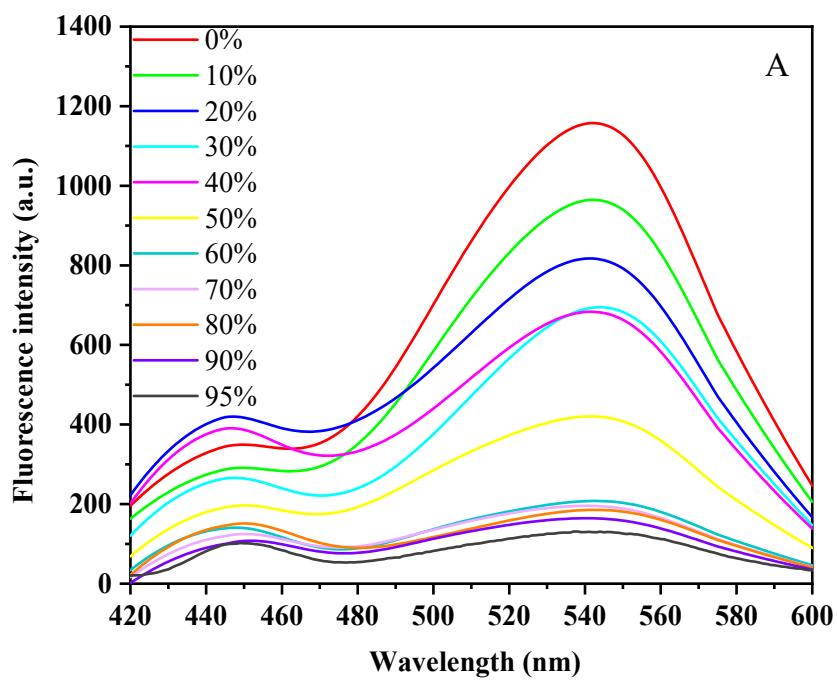


Figure S7 Fluorescence spectra of **AS-CPM** in DMSO-H₂O with different water contents (1.0 μ M, $\lambda_{\text{ex}} = 390$ nm)

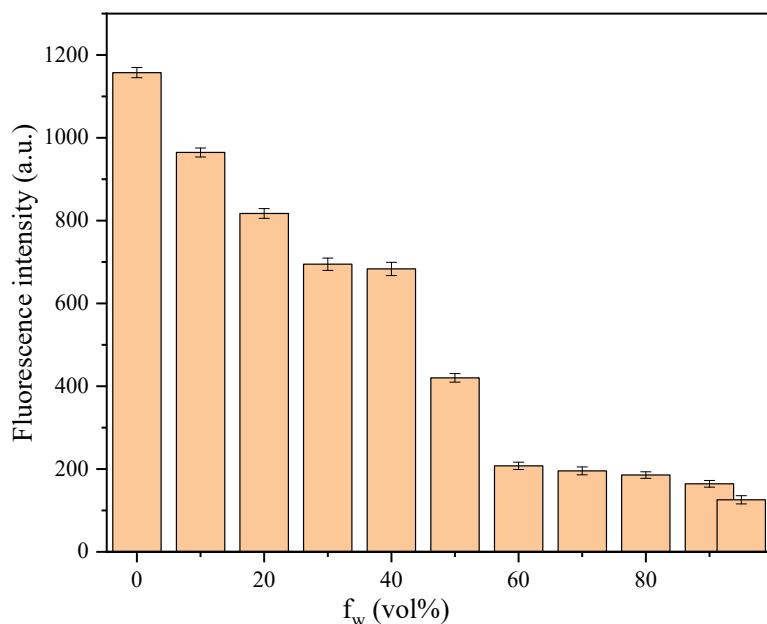


Figure S8 Maximum fluorescence intensities of **AS-CPM** in DMSO-H₂O with different water contents (1.0 μ M, $\lambda_{\text{ex}} = 390$ nm)

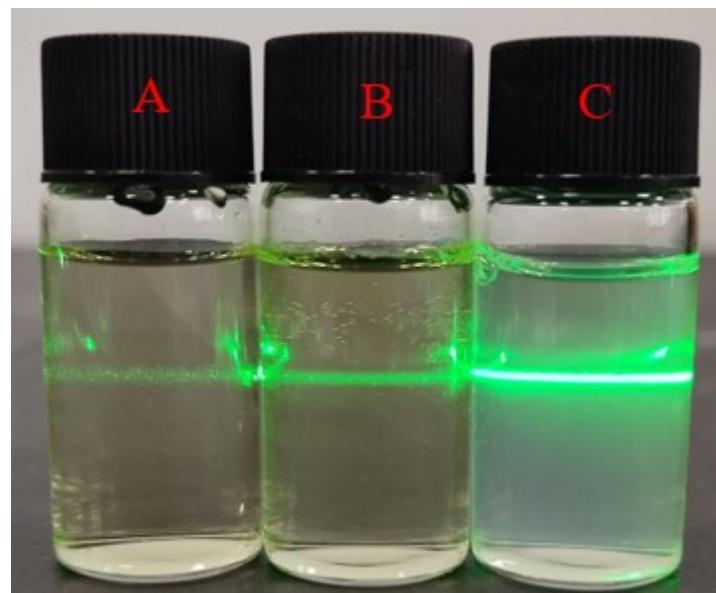


Figure S9 Tyndall experiments of (A) **AS-CPM** (1.0 μ M) in DMSO-H₂O solution (5:95), (B) **AS-CPM** (1.0 μ M) in DMSO and (C) **AS-CPM** (1.0 μ M) + quizalofop-p-ethyl (1.0 μ M) in DMSO-H₂O solution (5:95).

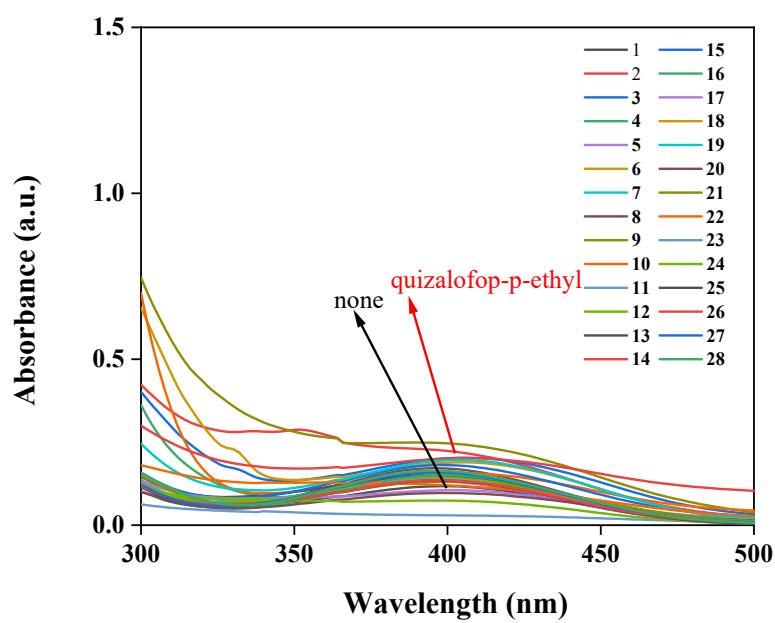


Figure S10 UV-vis spectra of probe **AS-CPM** (1.0 μ M) in the presence of various analytes (1.0 μ M) in DMSO-H₂O solution (5:95). 1 = none, 2 = quizalofop-p-ethyl, 3 = tribenuron methyl, 4 = imidacline, 5 = N-(Phosphonomethyl)glycine 2-propylamine

(1:1), 6 = monosulfuron, 7 = hymexazol, 8 = clopyralid, 9 = haloxyfop-P, 10 = 5-Ethyl-2-(4-isopropyl-4-methyl-5-oxo-1H-imidazolin-2-yl)nicotinic acid, 11 = 1-naphthaleneacetic acid, 12 = thifensulfuron methyl, 13 = tricyclazole, 14 = monosultap, 15 = Molosultap, 16 = spirosamine ethanolamine salt, 17 = metaldehyde, 18 = ethoxysulfuron, 19 = Na^+ , 20 = K^+ , 21 = Mg^{2+} , 22 = Ca^{2+} , 23 = Cu^{2+} , 24 = Zn^{2+} , 25 = CO_3^{2-} , 26 = NO_3^- , 27 = HCO_3^- , 28 = Cl^- .

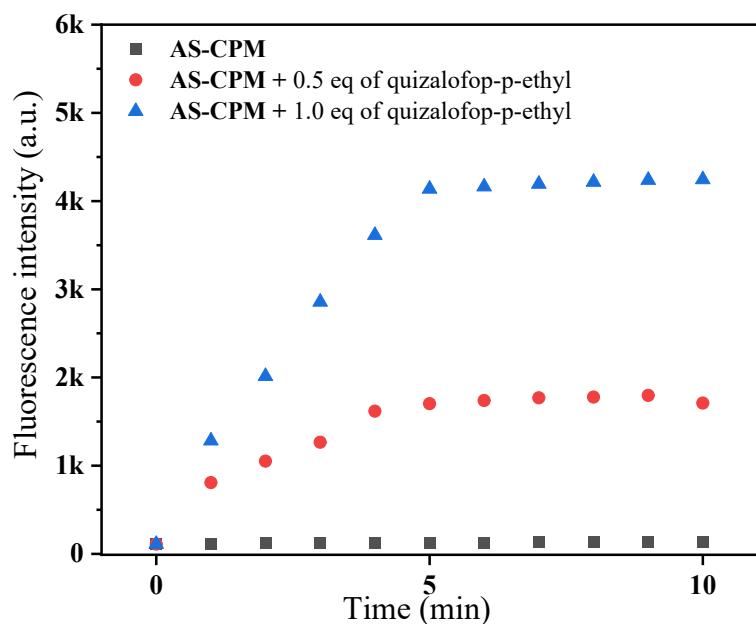


Figure S11 The plot of response time of **AS-CPM** (1.0 μM) in presence of quizalofop-p-ethyl (1.0 μM).

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

method	LOD	Reference
AuNP-LFIA	2.68×10^{-8} M	Sci total environ 2023 , 857, Part 1 DOI:10.1016/j.scitotenv.2022.15942 7
HPLC-MS/MS	M: 1.21×10^{-8} M P: 5.36×10^{-9} M	J Chromatogr A 2023 , 1707. DOI:10.1016/j.chroma.2023.464289
LC-MS/MS	2.01×10^{-8} M	Foods 2022 , 11 DOI:10.3390/foods11070899
GC-MS/MS	6.71×10^{-10} M	J Food Compos Anal 2023 , 115. DOI:10.1016/j.jfca.2022.105011
LC-MS/MS	Not mentioned	J Food Sci Tech Mys 2015 , 52, 4001-4014. DOI:10.1007/s13197-014-1473-9
2.98×10^{-8} M		Talanta 2024 ;276:126269. DOI: 10.1016/j.talanta.2024.126269 .
1.12×10^{-8} M		This work

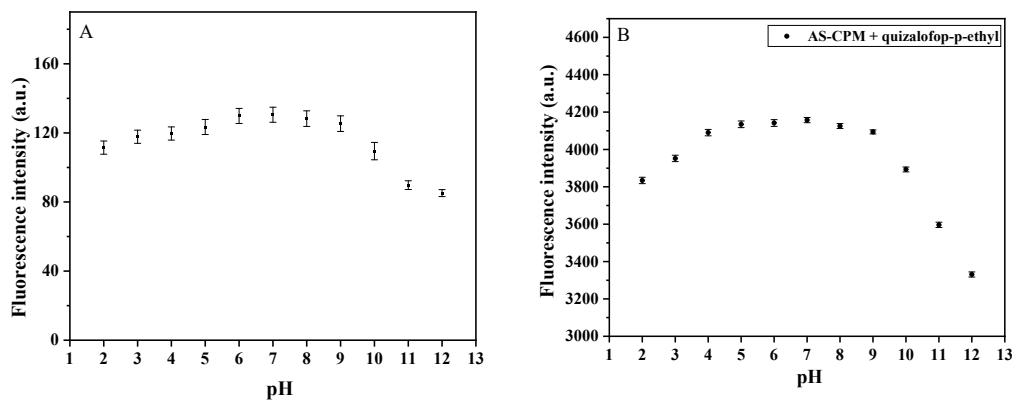


Figure S12 The influence of pH on the maximum fluorescence intensities of **AS-CPM** (A) and **AS-CPM + quizalofop-p-ethyl** (B). ($\lambda_{\text{ex}} = 390$ nm, 1.0 μM each in DMSO-H₂O (5:95)).

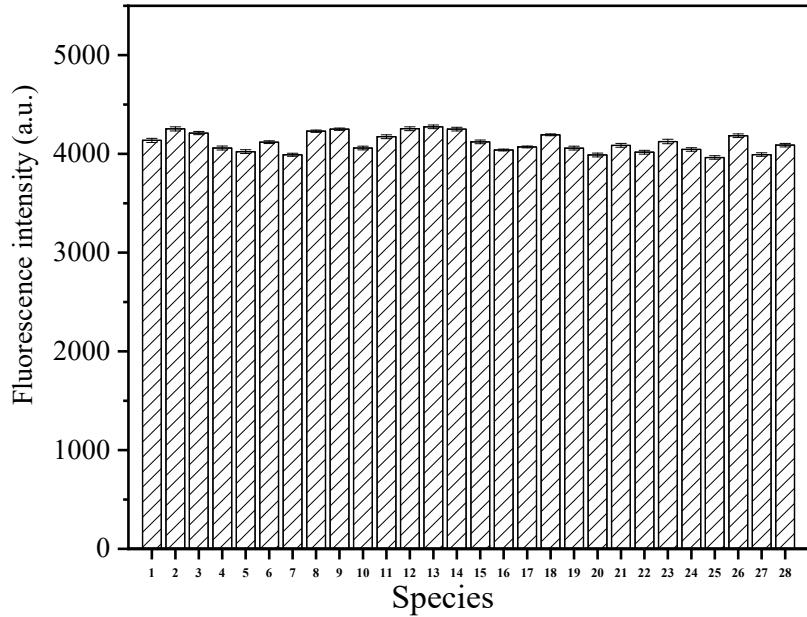


Figure S13 The interference experiments of **AS-CPM** (1.0 μM) with quizalofop-p-ethyl in presence of various interfering species (1.0 μM each, $\lambda_{\text{ex}} = 390$ nm) in DMSO-H₂O (5:95). 1 = **AS-CPM + quizalofop-p-ethyl**, 2 = 1 + quizalofop-p-ethyl, 3

= 1 + tribenuron methyl, 4 = 1 + imidacline, 5 = 1 + N-(Phosphonomethyl)glycine 2-propylamine (1:1), 6 = 1 + monosulfuron, 7 = 1 + hymexazol, 8 = 1 + clopyralid, 9 = 1 + haloxyfop-P, 10 = 1 + 5-Ethyl-2-(4-isopropyl-4-methyl-5-oxo-1H-imidazolin-2-yl)nicotinic acid, 11 = 1 + 1-naphthaleneacetic acid, 12 = 1 + thifensulfuron methyl, 13 = 1 + tricyclazole, 14 = 1 + monosultap, 15 = 1 + Molosultap, 16 = 1 + spirosamine ethanolamine salt, 17 = 1 + metaldehyde, 18 = 1 + ethoxysulfuron, 19 = 1 + Na^+ , 20 = 1 + K^+ , 21 = 1 + Mg^{2+} , 22 = 1 + Ca^{2+} , 23 = 1 + Cu^{2+} , 24 = 1 + Zn^{2+} , 25 = 1 + CO_3^{2-} , 26 = 1 + NO_3^- , 27 = 1 + HCO_3^- , 28 = 1 + Cl^- .

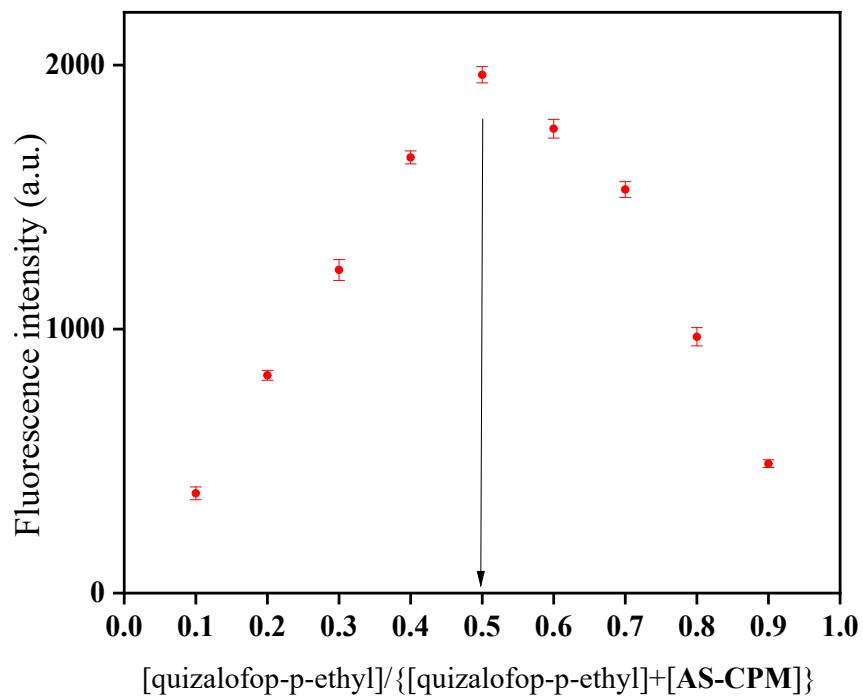


Figure S14 The Job's plot of **AS-CPM** with quizalofop-p-ethyl in DMSO- H_2O (5:95) ($\lambda_{\text{ex}} = 390$ nm) $[\text{quizalofop-p-ethyl}]+[\text{AS-CPM}] = 1.0 \mu\text{M}$.

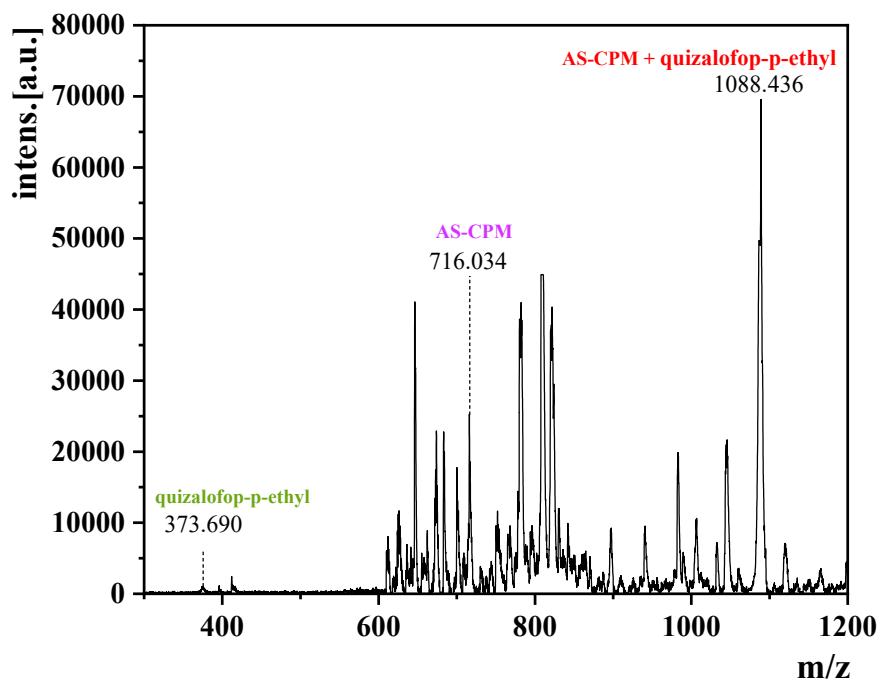


Figure S15 The binding MS spectrum for **AS-CPM** with quizalofop-p-ethyl.

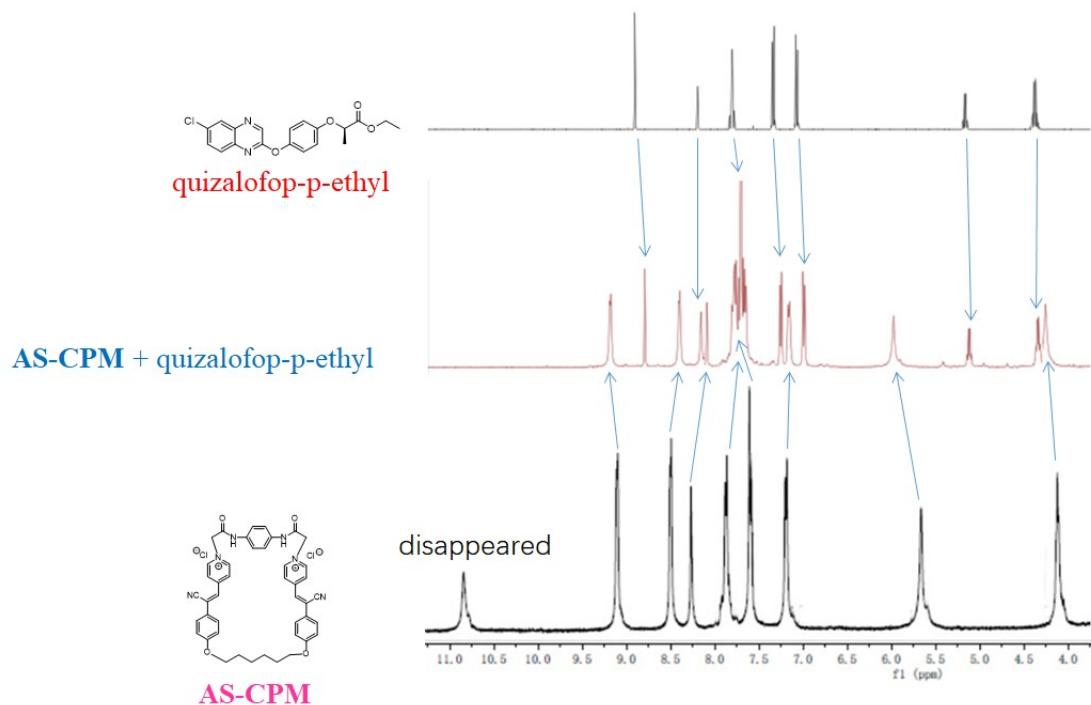


Figure S16 The binding ^1H NMR spectrum for **AS-CPM** with quizalofop-p-ethyl.

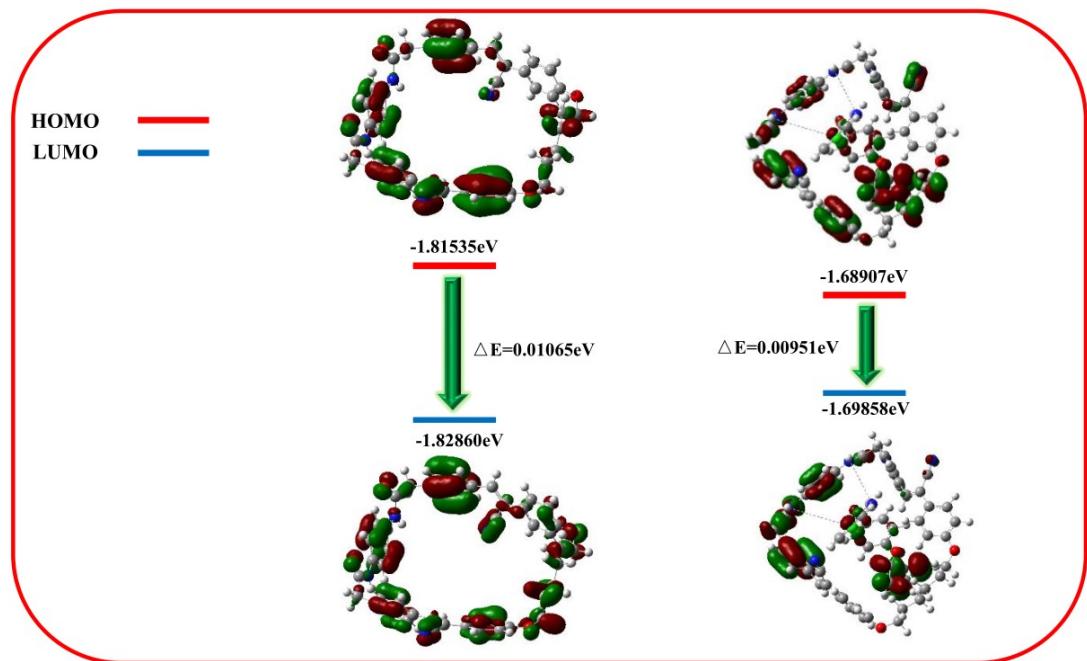


Figure S17 The energy level of HOMO and LUMO for AS-CPM (left) and AS-CPM with quizalofop-p-ethyl (right).

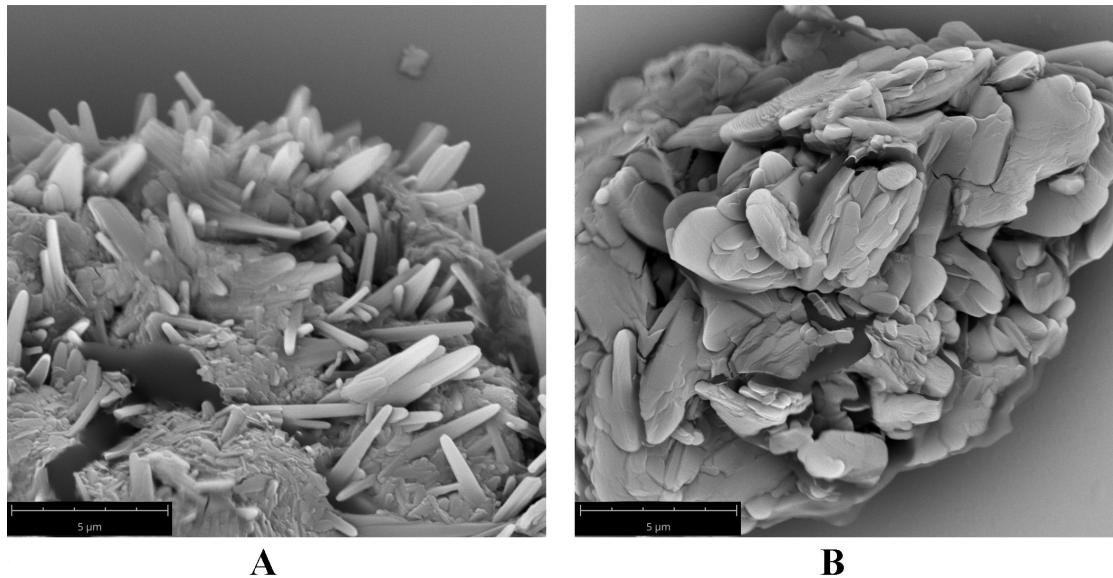


Figure S18 The SEM images of (A) AS-CPM and (B) AS-CPM + quizalofop-p-ethyl.

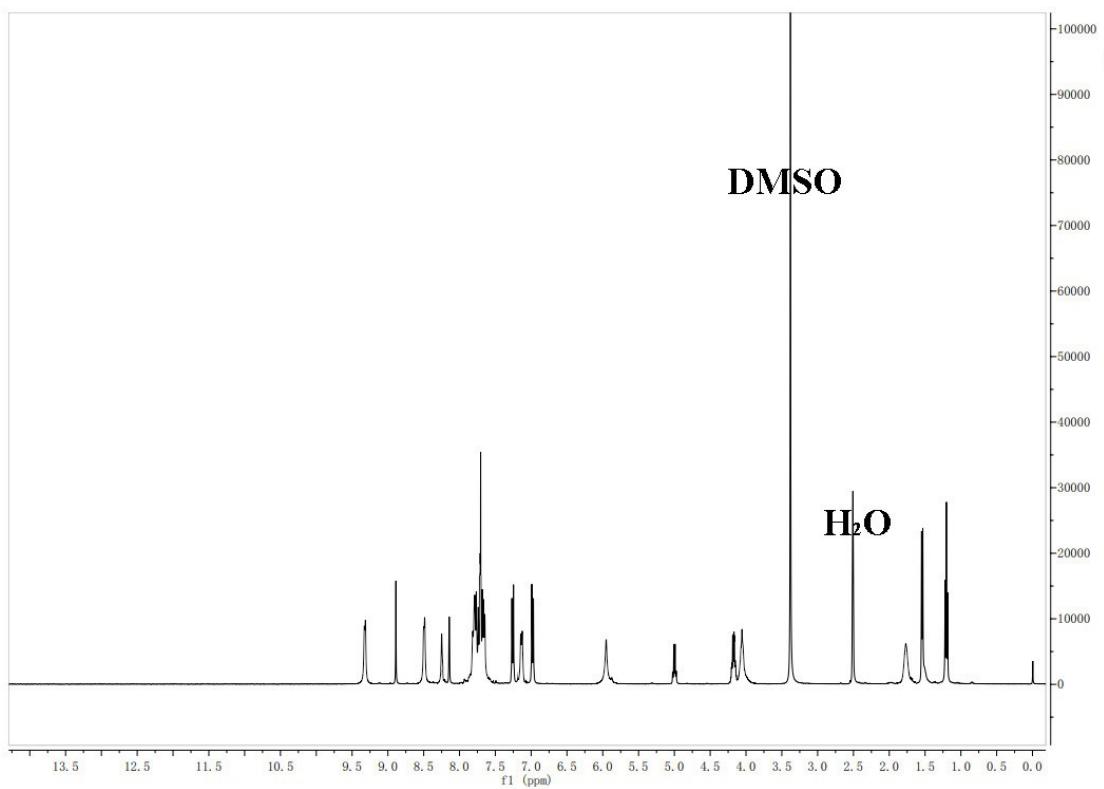


Figure S19 The full ^1H NMR spectrum of AS-CPM + quizalofop-p-ethyl in MDSO-d₆.