CuI-p-DPA coordination polymer isomers for "turn-on" fluorescent detection of thiophanate-methyl

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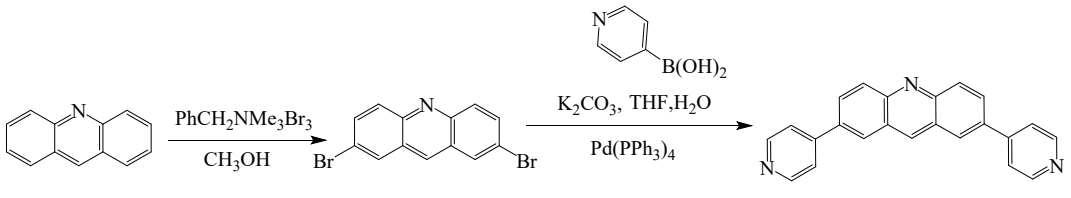
Synthesis of 2,7-di (pyridin-4-yl) acridine (p-DPA)

The 2,7-di (pyridin-4-yl) acridine (p-DPA) was synthesized by Suzuki coupling reaction. The synthetic route of p-DPA is shown in Fig. S1. Benzyltriethylammonium bromide (12 g, 44 mmol) and acridine (2.16 g, 12 mmol) were placed in a round bottom flask, dissolved in 100 mL methanol and stirred at 60 °C for 16 hours. After cooling to room temperature, the crude products obtained by filtration were washed with a small amount of pyridine and dichloromethane. After vacuum drying at 50 °C, the pale yellow solid 2,7-dibromoacridine was obtained. Then 2,7-dibromoacridine (500 mg, 1.48 mmol), pyridine-4-boronic acid (455.9 mg, 3.71 mmol) were dissolved in 100 mL tetrahydrofuran (THF) solution and added to the round bottom flask. 2 g K_2CO_3 was dissolved in 10 mL water and added to the solution. Next, $Pd(PPh_3)_4$ (0.13 g, 0.12 mmol) was added to the solution and quickly degassed three times. The solutions were stirred at 70 °C for three days under N_2 atmosphere. After the reaction stopped and cooled to room temperature, the solvents were removed by rotary evaporation, and the obtained products were extracted with water and dichloromethane three times. The extracted dichloromethane solutions were dried with anhydrous sodium sulfate and then removed by rotary evaporation to obtain the crude product. Lastly, the crude products were purified by silica gel column chromatography with gradient elution using methanol and dichloromethane as eluents. The obtained yellow powders were p-DPA, and the yield of the reaction was 45 %. NMR spectrums are shown in Fig. S2 and Fig. S3.

^{1}H-NMR (600 MHz, DMSO-d_6) δ (ppm): 9.15 (s, 1H), 8.70 (d, J = 5.0 Hz, 4H), 8.60 (s, 2H),

8.22 (s, 4H), 7.88 (d, J = 4.5 Hz, 4H).

^{13}C-NMR (101 MHz, DMSO-d_6) δ (ppm): 150.89, 149.25, 146.42, 138.55, 134.85, 130.46, 130.09, 127.53, 126.85, 121.96.



2,7-di(pyridin-4-yl)acridine

p-DPA

Fig. S1 Synthetic route of p-DPA.

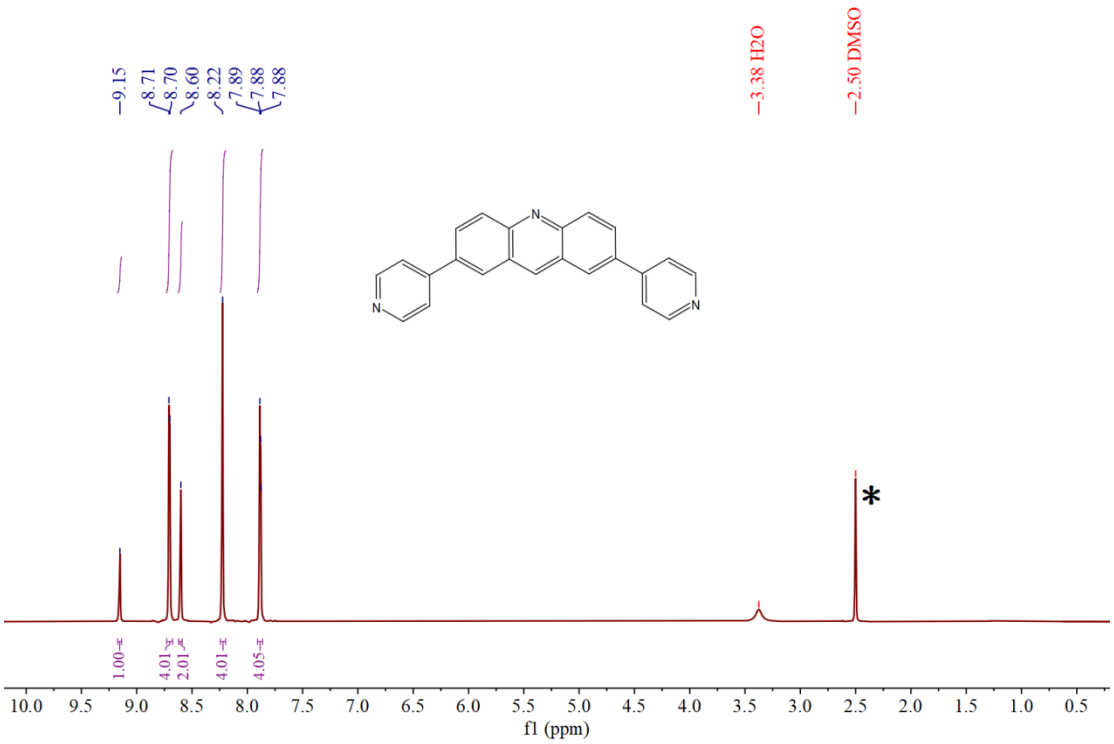


Fig. S2 ^{1}H NMR (600 MHz, DMSO-d_6) spectrum of p-DPA.

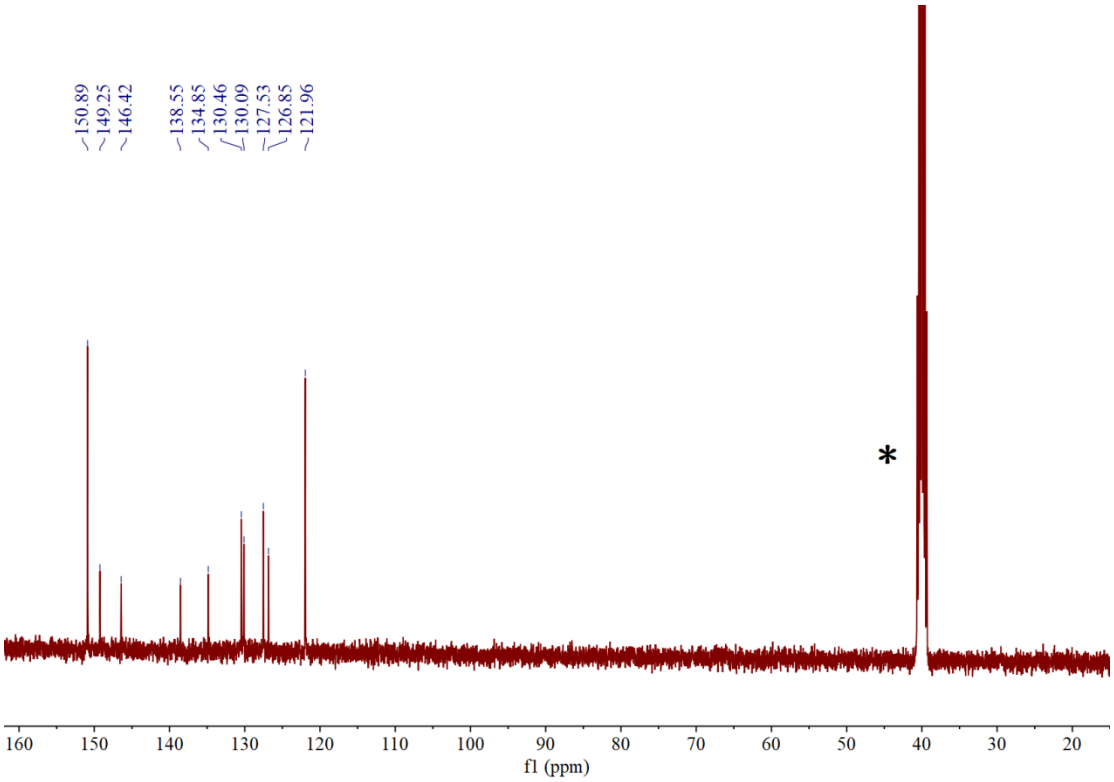


Fig. S3 ^{13}C NMR (101 MHz, DMSO-d_6) spectrum of p-DPA.

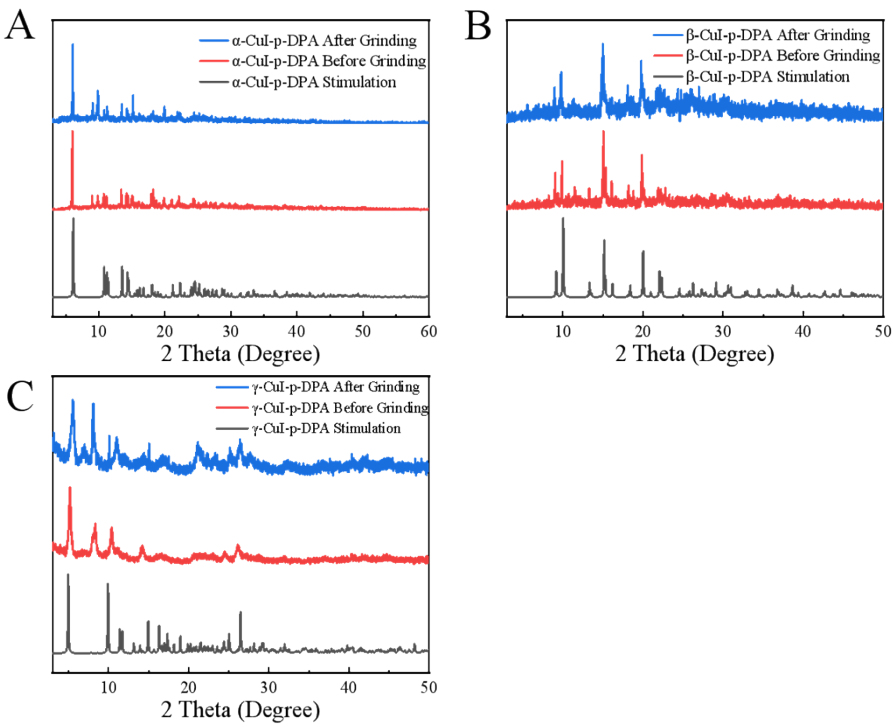


Fig. S4 PXRD spectra of (A) α-CuI-p-DPA, (B) β-CuI-p-DPA and (C) γ-CuI-p-DPA before and after grinding.

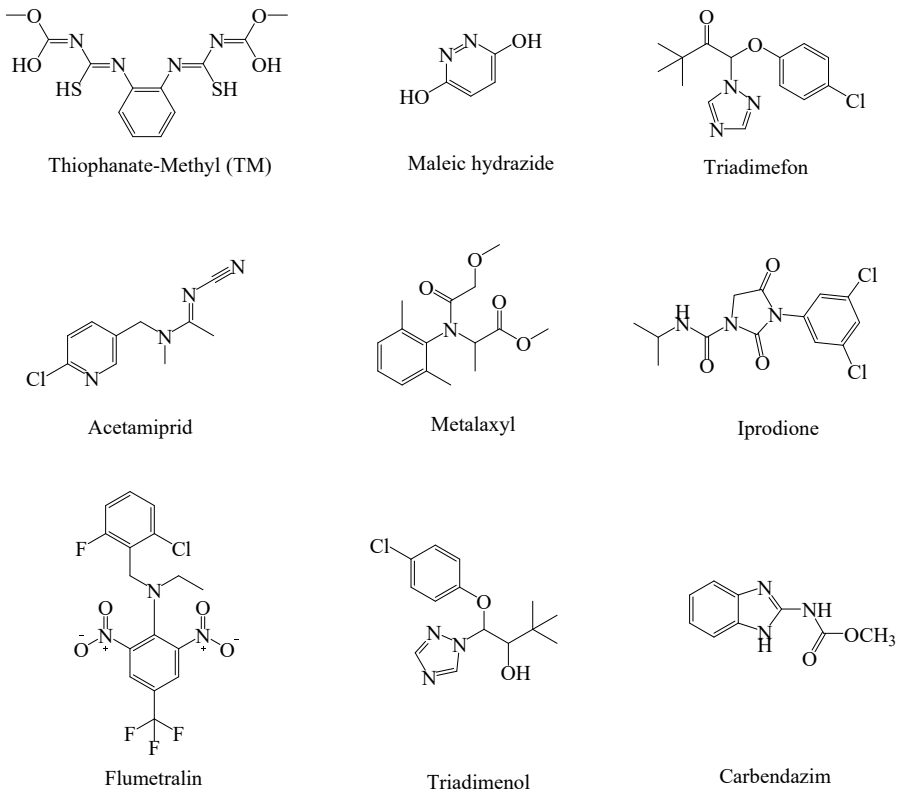


Fig. S5 The structures of thiophanate-methyl (TM), Maleic hydrazide, triadimefon, acetamiprid, metalaxyl, iprodione, flumetralin, triadimenol and carbendazim.

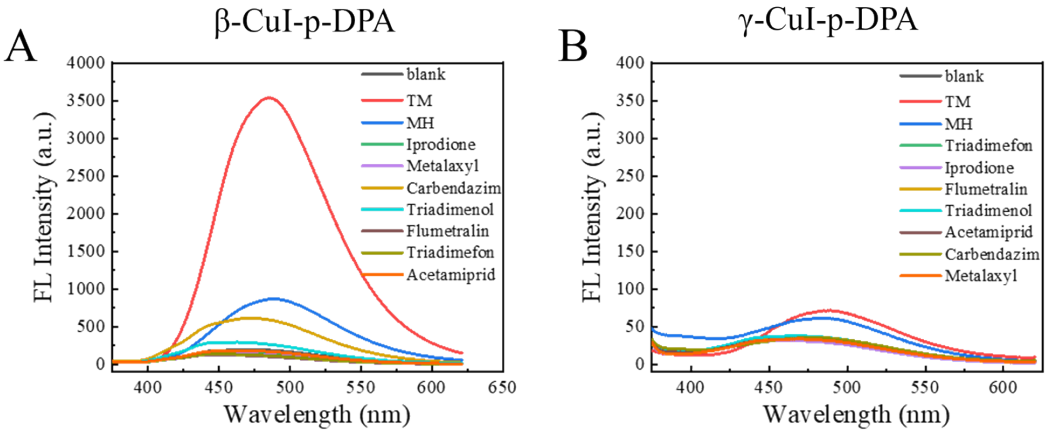


Fig. S6 The fluorescence spectra of (A) β-CuI-p-DPA and (B) γ-CuI-p-DPA after interaction with different pesticides.

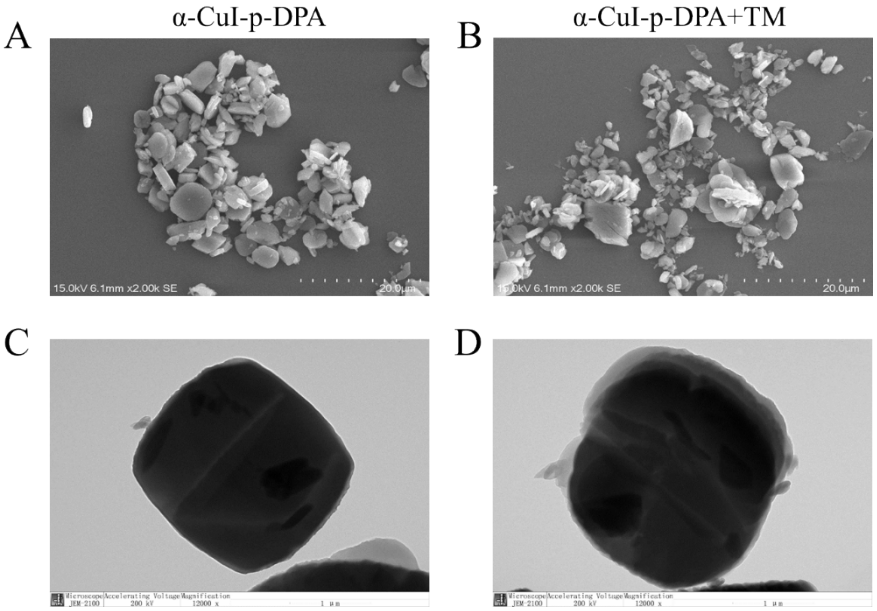


Fig. S7 Scanning electron microscope images of α-CuI-p-DPA (A) before and (B)after incubation with TM. Transmission electron microscopy images of α-CuI-p-DPA (C) before and (D) after treated with TM.

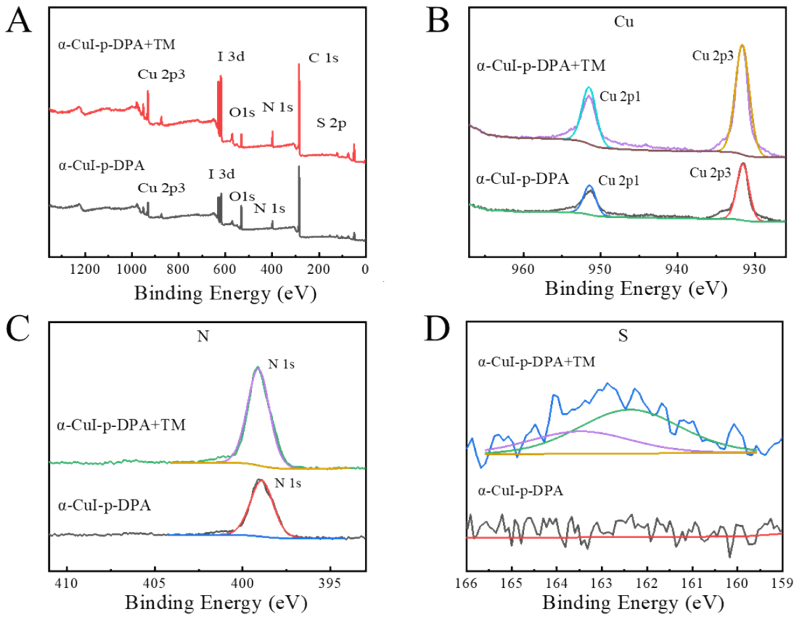


Fig. S8 The full scan XPS spectrum of α-CuI-p-DPA before and after incubation with TM. High-resolution XPS spectra for (B) Cu 2p, (C) N 1s and (D) S 2p regions of α-CuI-p-DPA before and after incubation with TM.

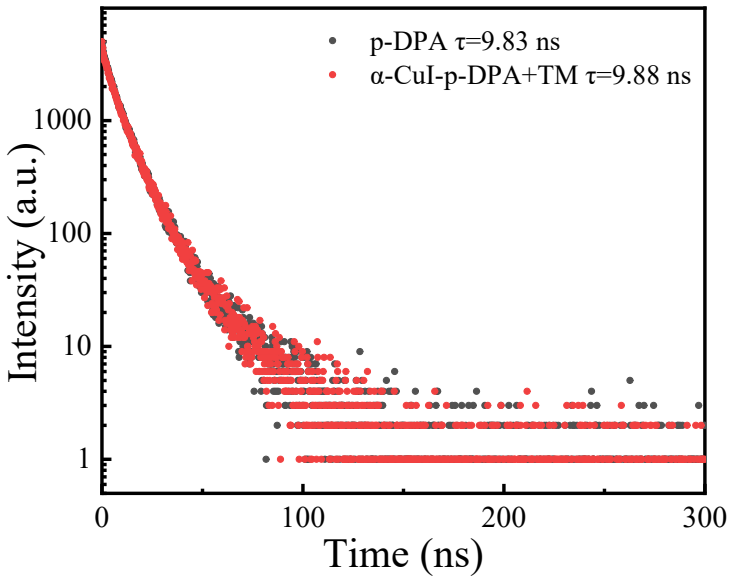


Fig.S9 The fluorescence lifetimes of α-CuI-p-DPA supernatants before and after the incubation with TM

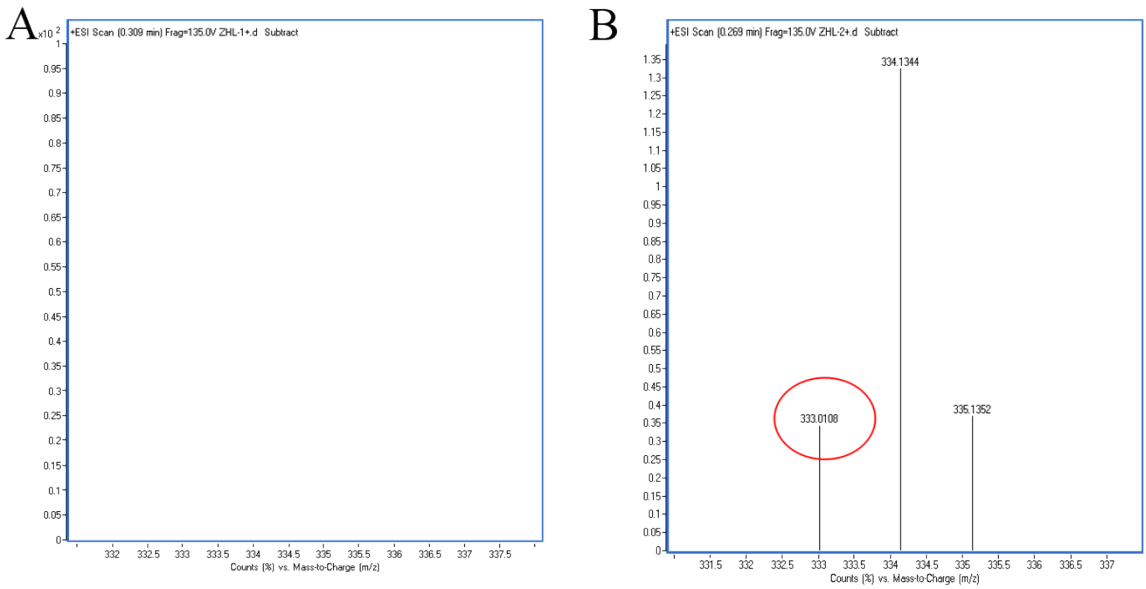


Fig. S10 The high-resolution mass spectrometry of the α-CuI-p-DPA supernatant (A) before and (B) after the incubation with TM.