

Supplementary Information

A Novel Fluorescent Probe of Alkyne Compounds for Putrescine Detection based on Click Reaction

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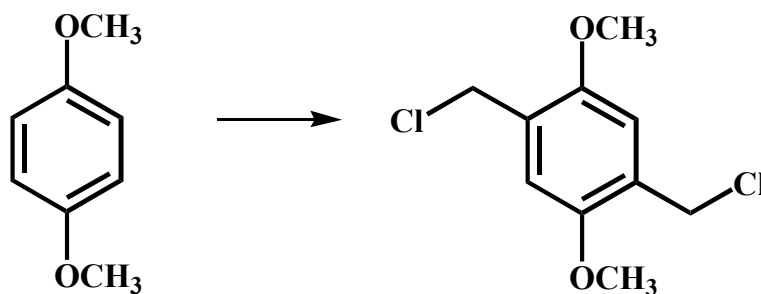
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1. Synthesis

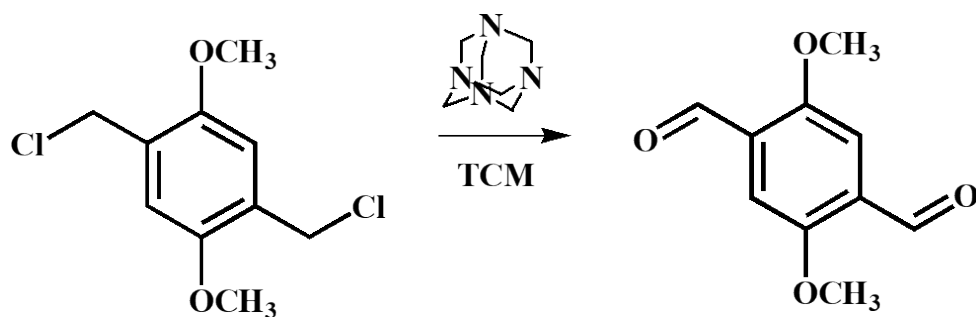
1.1 Synthesis of compound 1



Scheme S1. The synthetic process of compound 1

1,4-dimethoxybenzene (2.0 g, 14.46 mmol), formaldehyde solution (10 mL, 37wt%) and paraformaldehyde (0.6 g, 20 mmol) were added to 1,4-dioxane solution (6 mL). The resulting mixture was heated to 90°C. Then concentrated HCl (37 wt%, 2 mL) was added dropwise. After heating for 1h, concentrated HCl (37 wt%, 6 mL) was added again, and the mixture was cooled to room temperature to obtain white precipitate. The filter residue was washed with ultrapure water and then dried in vacuum. The crude product was recrystallized with acetone to obtain 2.38g white powder with a yield of 70%.¹ H NMR (400 MHz, CDCl₃) δ = 3.89 (s, 6H), 4.64 (s, 4H), 7.21 (s, 2H) ppm. FT-IR (KBr, cm⁻¹): 2981(-CH₃), 2859(C-H), 1218(C-O-C), m.p.: 165.5°C.

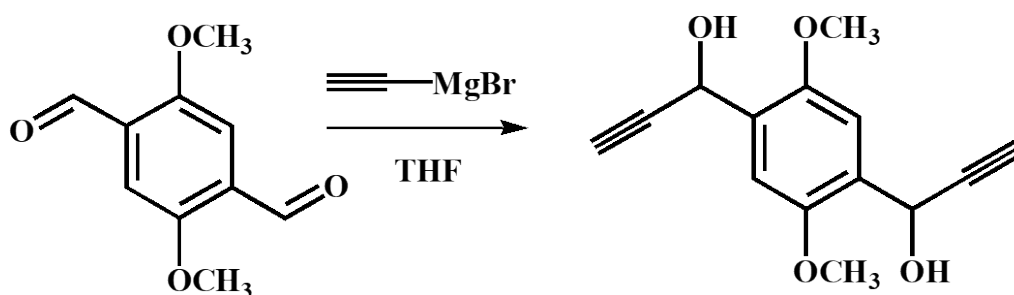
1.2 Synthesis of Compound 2



Scheme S2. The synthetic process of compound 2

Compound 1 (3.65 g, 15.6 mmol) and urotropine (4.02 g, 28.7 mmol) were dissolved in chloroform (35 mL) and stirred at 90°C for 24 h. After cooling to room temperature, the pale yellow precipitate was collected by filtration. Wash with chloroform several times and dissolve in water after drying. The aqueous solution was acidified with glacial acetic acid (8 mL) and stirred at 90°C for another 24 h. After the mixture was cooled to room temperature, then extracted with dichloromethane, the organic phase was collected and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation and the residual was recrystallized with EtOH to obtain yellow solid with a yield of 55%. ¹H NMR (400 MHz, d₆-DMSO) δ (ppm): 10.39 (s, 2H), 7.44 (s, 2H), 3.93 (s, 6H). FT-IR (KBr, cm⁻¹): 2958 (-CH₃), 2869 (C-H), 1679 (C=O), 1213 (C-O). m.p.: 175.6°C.

1.3 Synthesis of compound 3



Scheme S3. The synthetic process of compound 3

Compound 2 (0.98 g, 4 mmol) and the dehydrated THF (40 mL) were added to a three-necked flask. Under the protection of nitrogen, the mixed solution was cooled to 0°C, and ethynyl magnesium bromide tetrahydrofuran solution (0.5 M, 20 mL) was added dropwise with stirring. The mixture was stirred overnight at room temperature under nitrogen protection, and then quenched by adding saturated aqueous ammonium chloride solution. The reaction mixture was extracted with DCM, and dried over anhydrous magnesium sulfate. After filtering and evaporating the solvent, 0.44 g of a yellow solid was obtained with a yield of 40%.

FT-IR (KBr, cm^{-1}): 3280 (-OH), 2110 ($\text{C}\equiv\text{C}$). ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.36(s,2H), 5.73 (s,2H), 3.98 (s,6H), 3.10 (s,2H), 2.73 (d, $J=10.8\text{Hz}$, 2H). m.p.: 179.4°C.

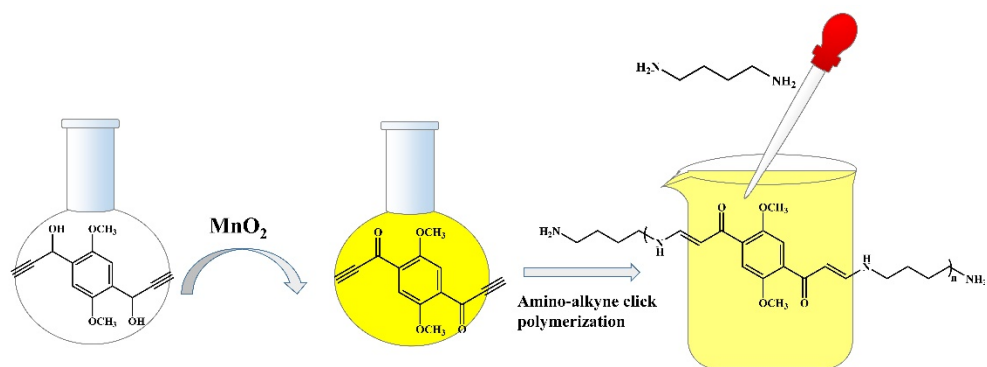


Figure S1. The schematic diagram of the synthetic experimental device

2. Spectral Characterization

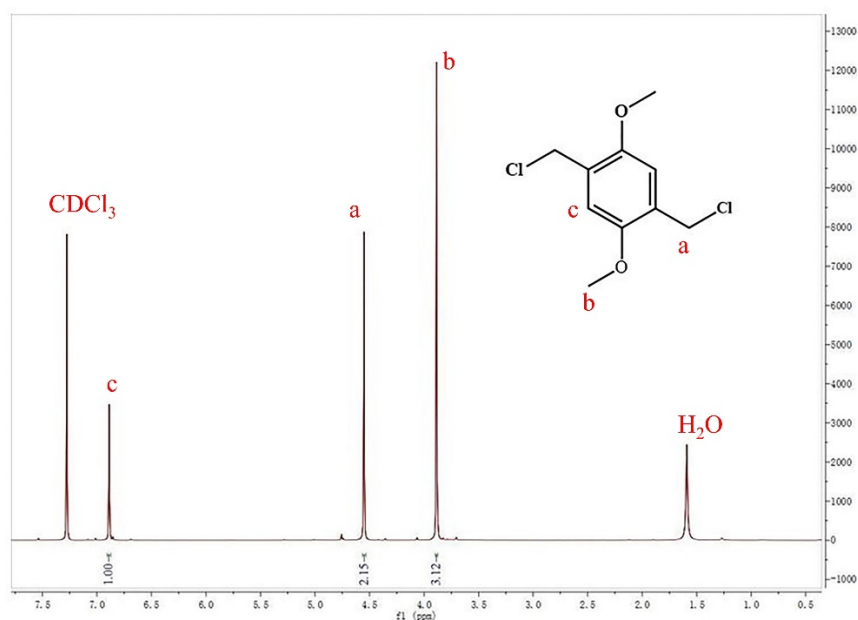


Figure S2. The ^1H NMR spectrum of compound 1 in CDCl_3 at 298 K

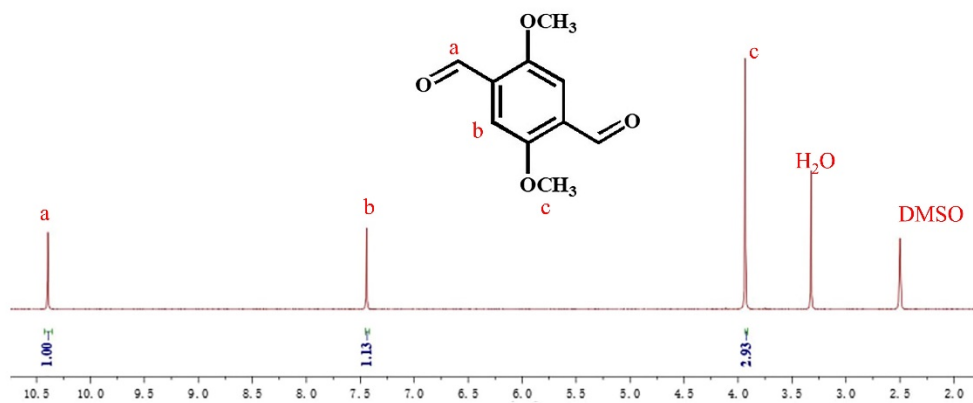


Figure S3. The ^1H NMR spectrum of compound 2 in DMSO at 298 K

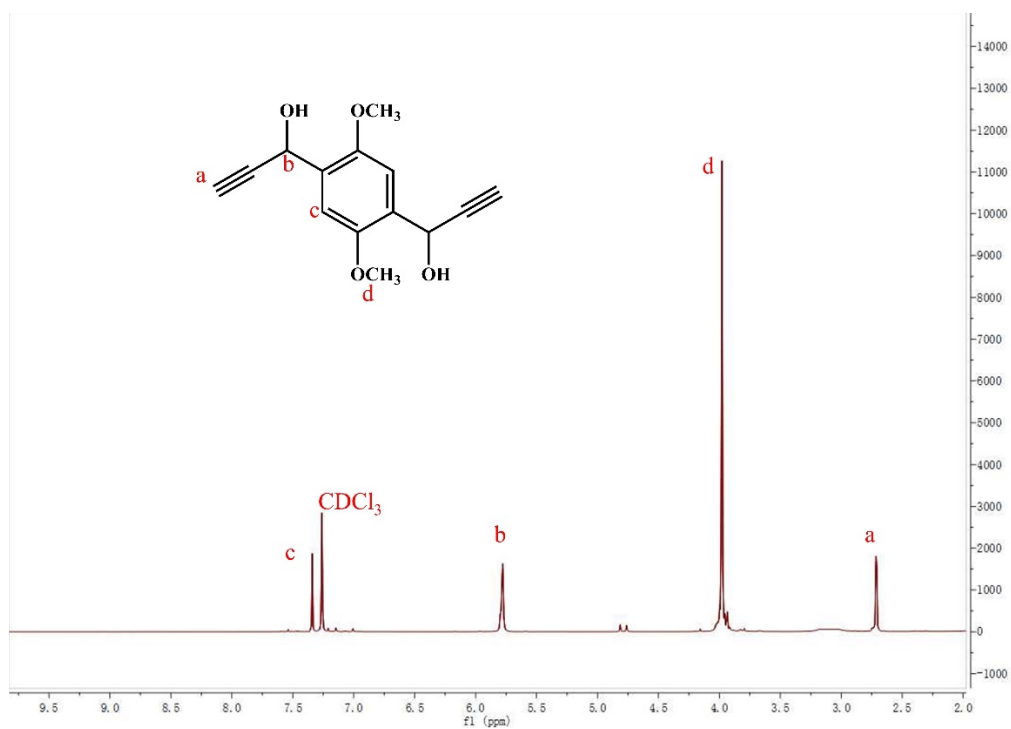


Figure S4. The ^1H NMR spectrum of compound 3 in CDCl₃ at 298 K

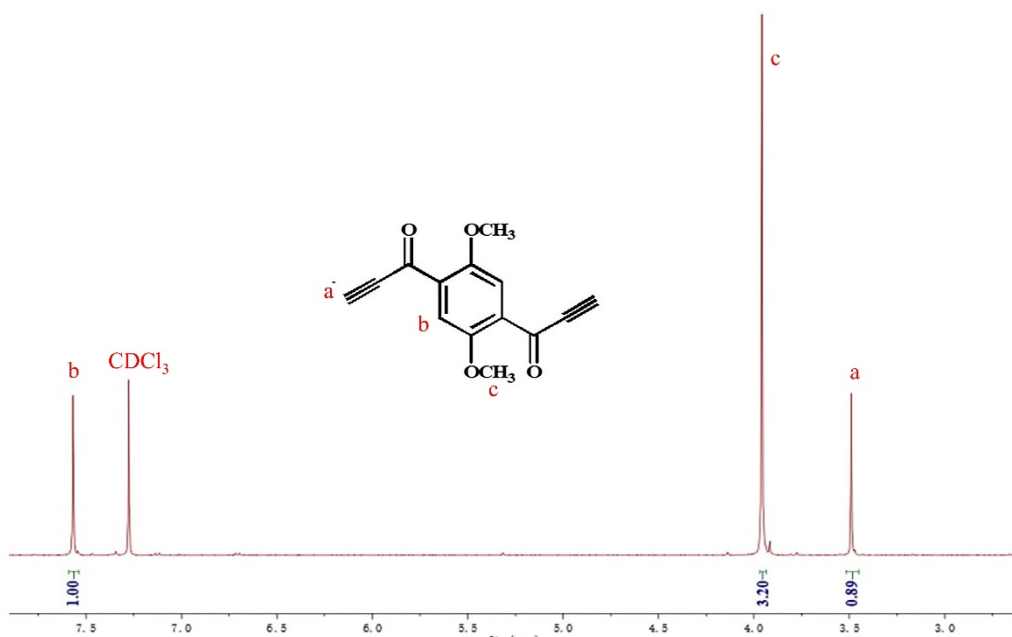


Figure S5. The ^1H NMR spectrum of DPY in CDCl_3 at 298 K

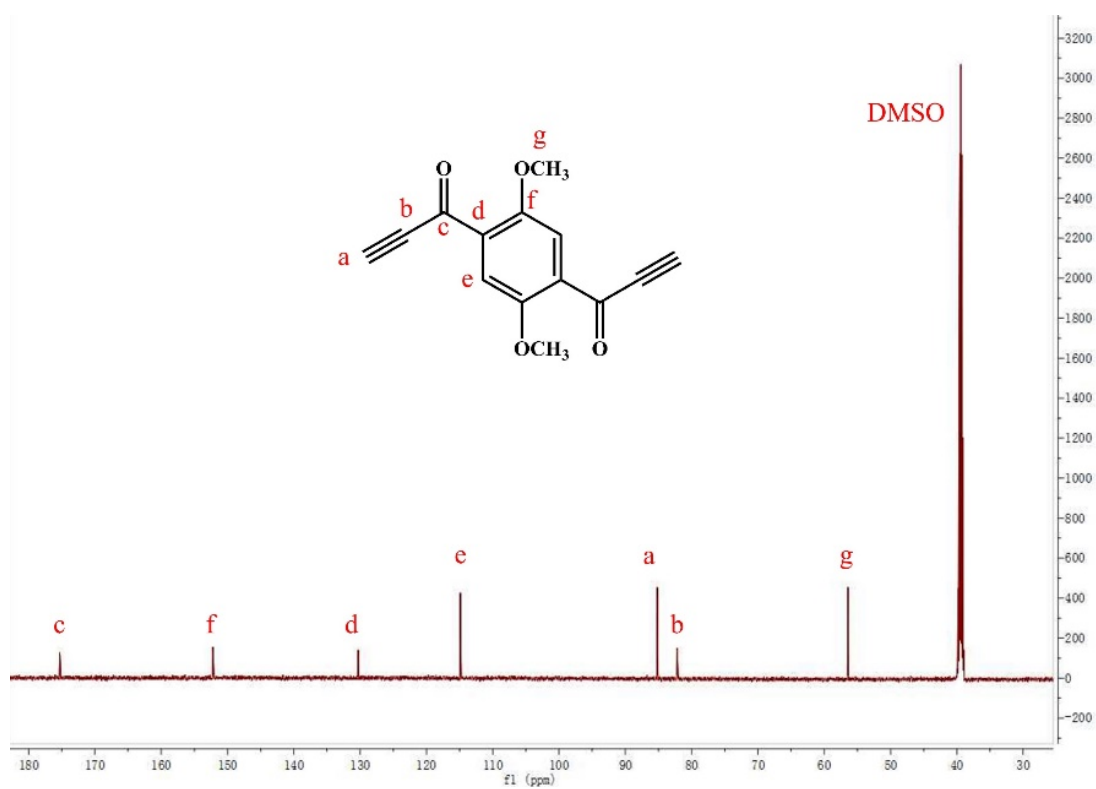


Figure S6. The ^{13}C NMR spectrum of DPY in DMSO-d₆ at 298 K

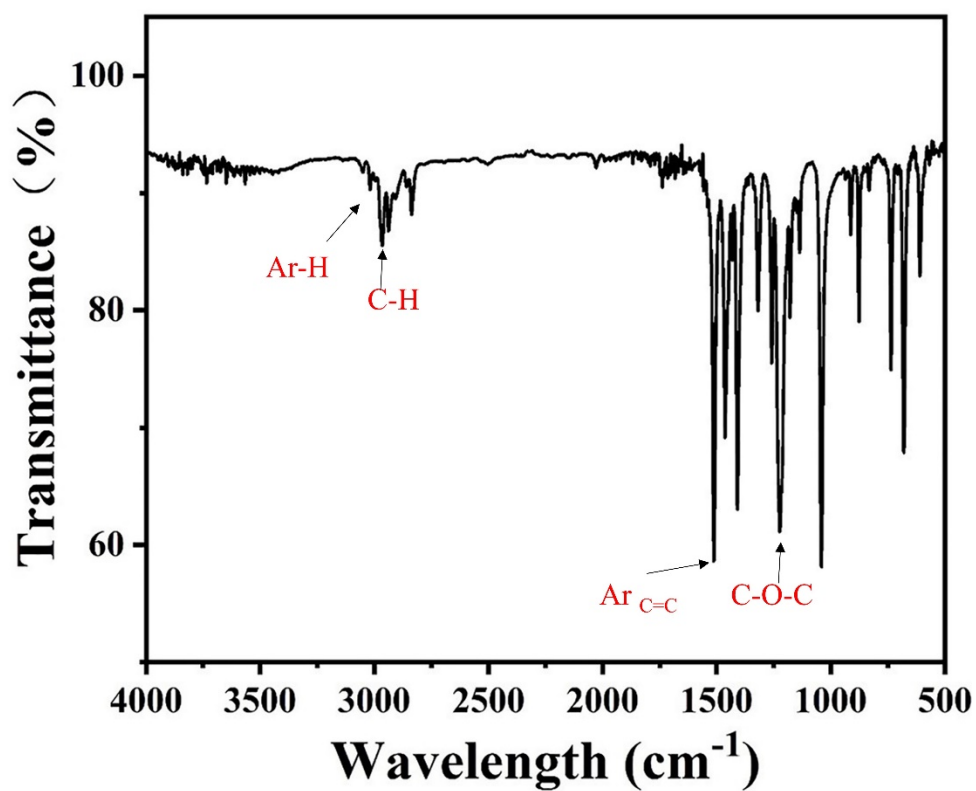


Figure S7. The FT-IR spectrum of compound 1

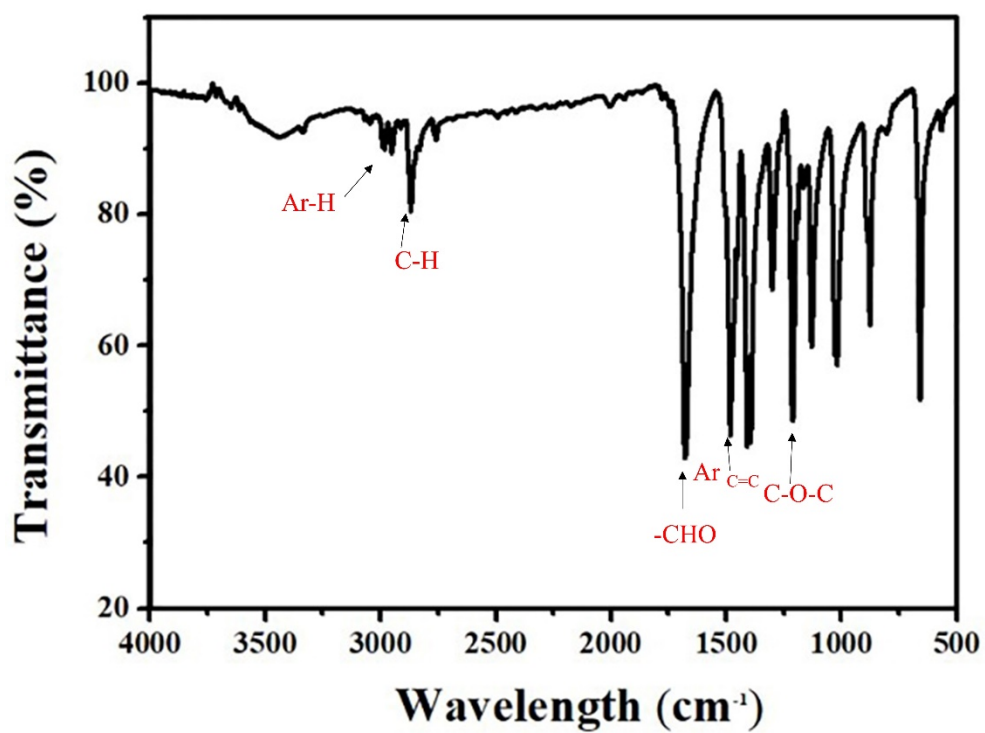


Figure S8. The FT-IR spectrum of compound 2

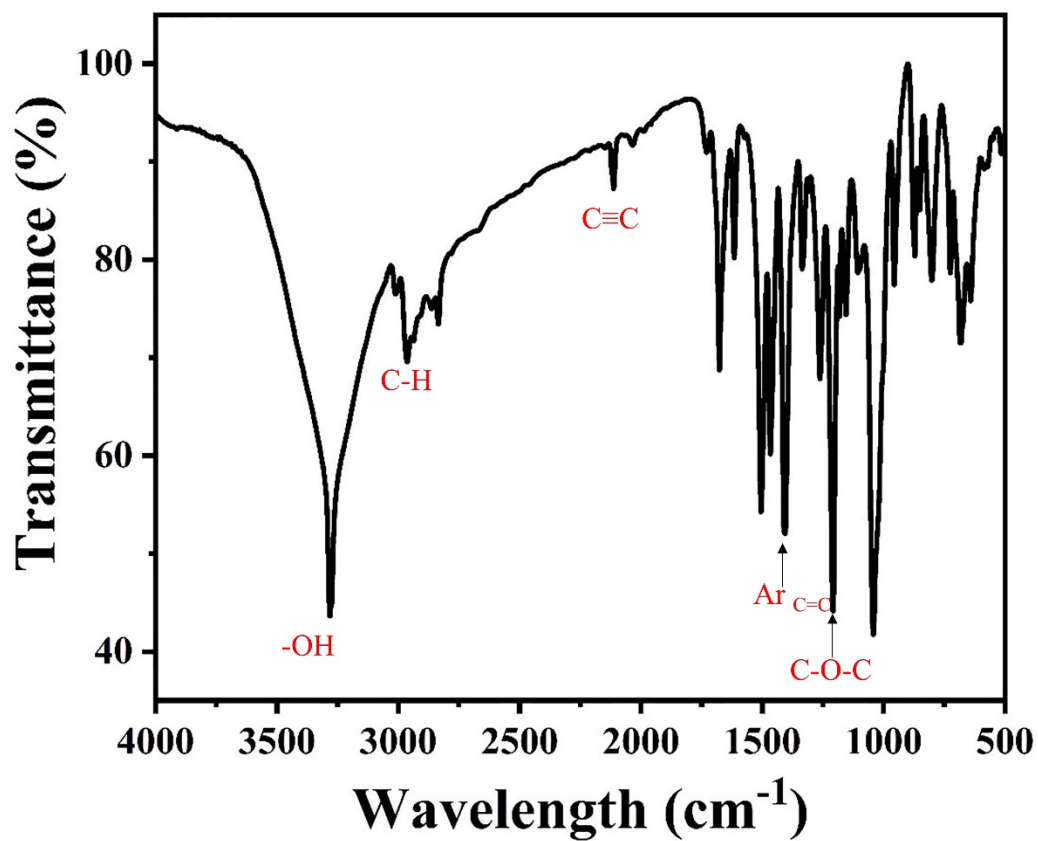


Figure S9. The FT-IR spectrum of compound 3

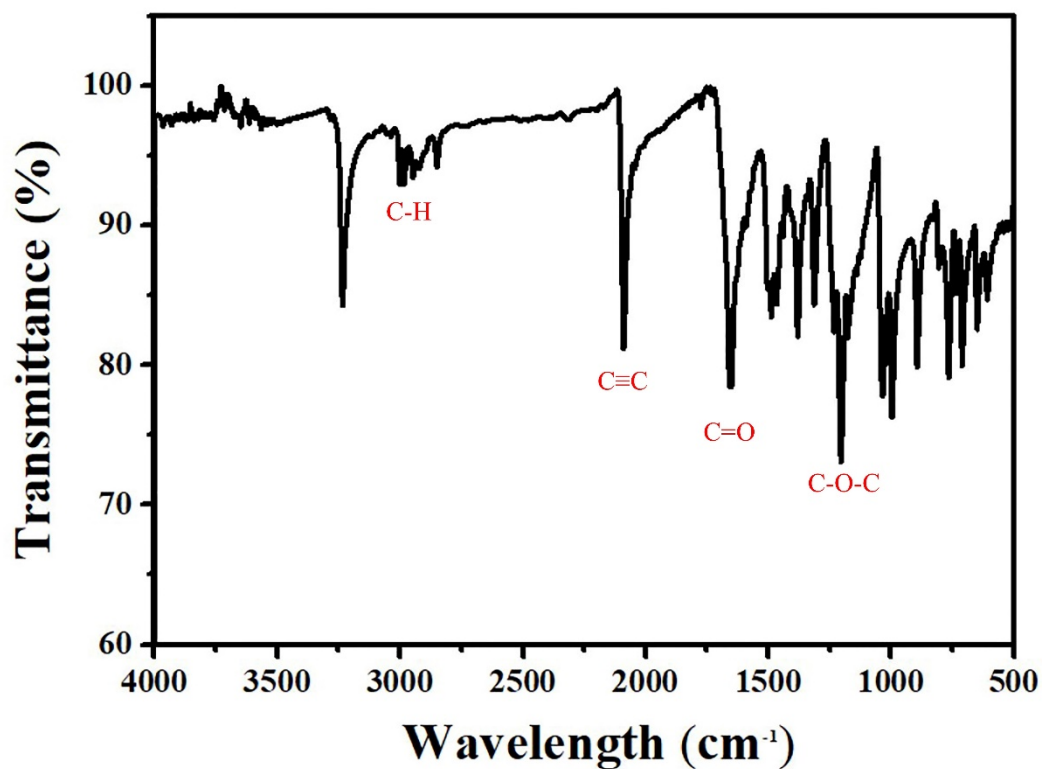


Figure S10. The FT-IR spectrum of DPY.

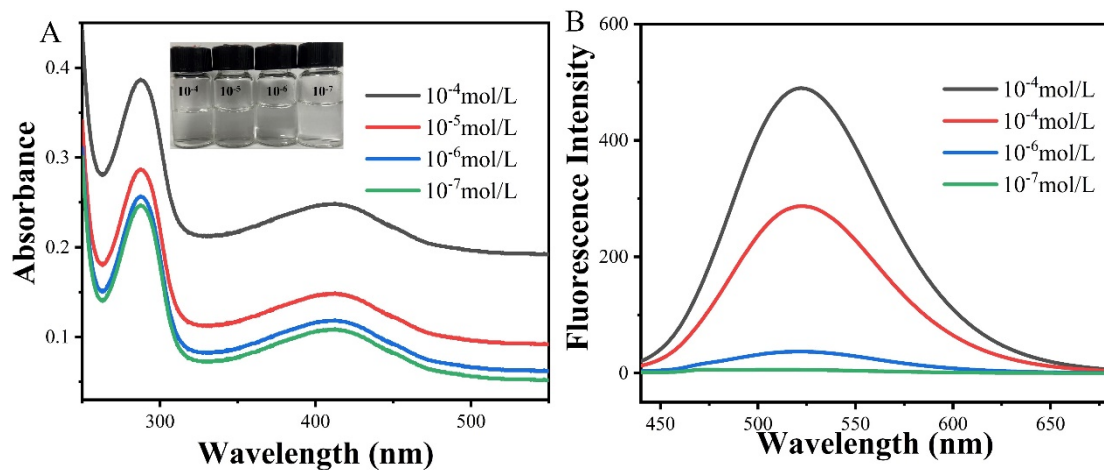


Figure S11. Ultraviolet absorption (A) and fluorescence emission (B) spectra of different concentrations of DPY from 0.1 μ M ~100 μ M in water.

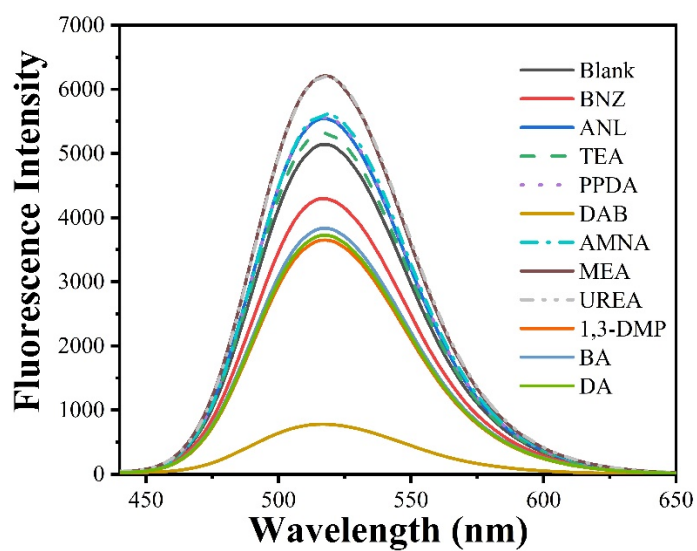


Figure S12. Fluorescence emission spectra of DPY to different amines.

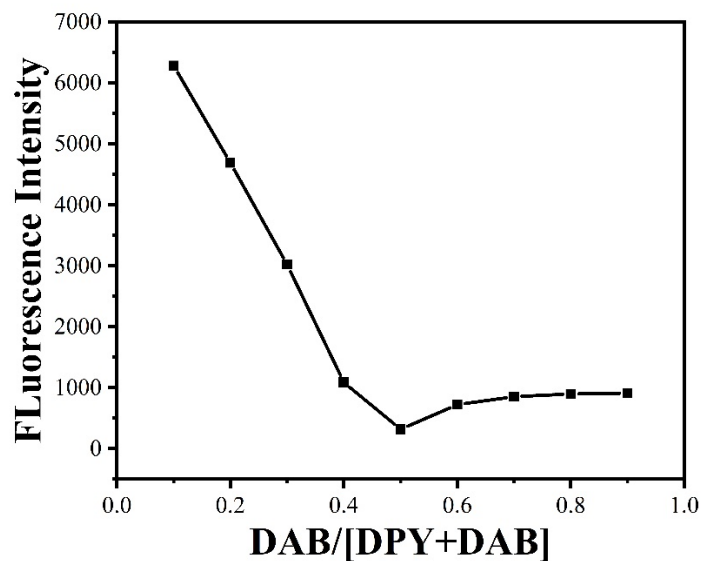


Figure S13. The Job's plot for DPY-DAB polymerization, $[\text{DPY}] + [\text{DAB}] = 10^{-5} \text{ mol/L}$.

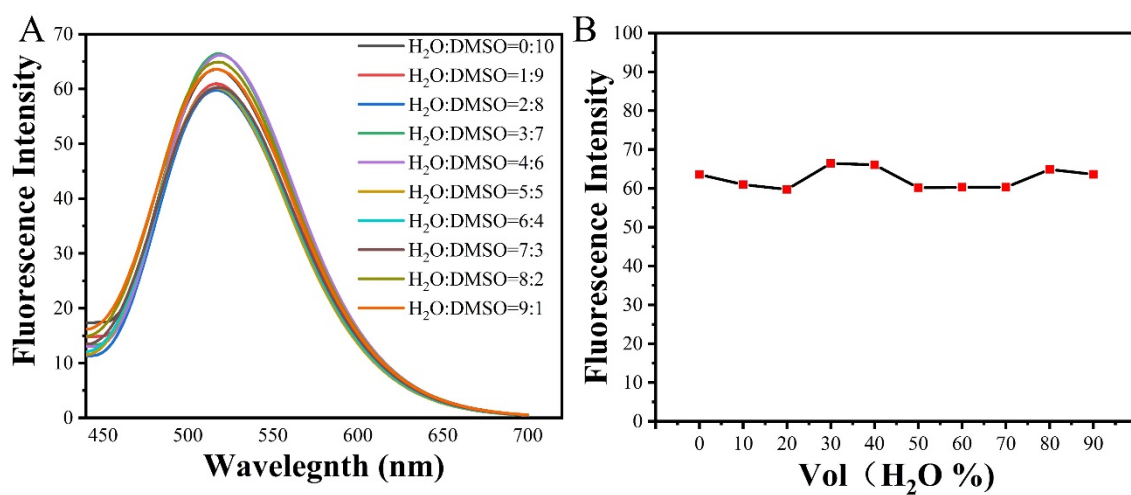


Figure S14. (A) Fluorescence changes of product by polymerization ($1 \times 10^{-5} \text{ mol/L}$) under different ratios of $\text{H}_2\text{O}/\text{DMSO}$; (B) Trend of fluorescence intensity of product by polymerization.