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A ratiometric, colorimetric fluorescent probe with a large emission shift for the fast detection of diethyl chlorophosphate

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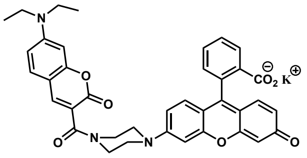
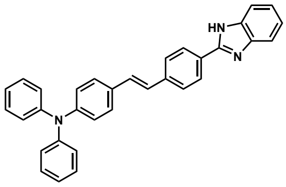
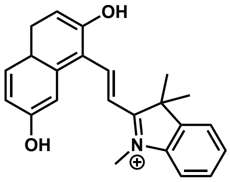
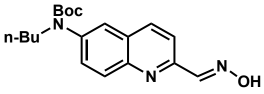
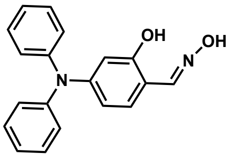
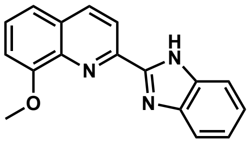
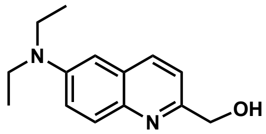
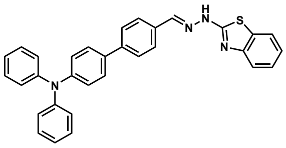
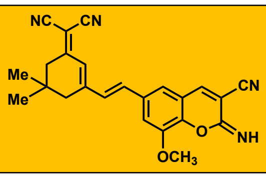
1. Ratiometric fluorescent probes for the detection of DCP.

Table S1. Comparison of **SWJT-16** with other ratiometric fluorescent probes for DCP

Probe		Ex/ Em (nm)	Response time	Reference
A		Ex= 410 Em= 460/536	Within 1 min	31
B		Ex= 390 Em= 483/573	40 s	32
C		Ex= 354 Em= 478/602	Within 1 min	33
D		Ex= 390 Em= 400/500	Within 10 min	34
E		Ex= 379 Em= 463/532	Within 30 s	35
F		Ex= 346 Em= 405/471	30 s	36
G		Ex= 320 Em= 382/488	60 min	37
H		Ex= 375 Em= 428/505	25 s	38
SWJT-16		Ex= 470 Em= 554/728	6 s	This work

2. General Methods.

2.1 Materials and Reagents

All regents used in the experiments such as isophorone, malonitrile, vanillin were purchased from Innochem company, China. All solvents can be used directly without further purification, which were purchased from Tianjin Tianzheng Fine Chemical Reagent Factory. DMSO for fluorescence detection was spectroscopic pure.

2.2 **Measurements**

^{1}H, ^{13}C NMR spectra were measured by Bruker-Avb-400M spectrometer using TMS as internal parameters. LC-MS spectra were recorded on the Waters e2695 spectrometer and chromatographic grade methanol was used as the solvent. Fluorescence spectra were obtained using a Hitachi-F7000 fluorescence spectrometer. All photographs under UV light were illuminated using a 365 nm handheld UV lamp.

2.3 The preparation of the test stock solution

The solution of SWJT-16 (1.0 mM) was prepared in Dimethyl sulfoxide. Other solutions (0.1 M) were prepared in N, N-Dimethylformamide (DMF), such as Diethyl chlorophosphite (DCP), 2-diethoxyphosphorylacetonitrile (DCMP), Triethyl phosphite (TEP). 20.0 μL of the SWJT -16 stock solution into test tube and diluting to 2.0 mL with organic solvent, followed by the addition of a moderate amount of nerve mimics stock solution. The mixture was then poured into a colorimetric dish and excited at 470 nm to obtain fluorescence spectra. The fluorescence quantum yield was determined with Rhodamine B as the standard.

The formula is as follows:

$$Y_u = Y_s \times \frac{F_u}{F_s} \times \frac{A_s}{A_u}$$

Where Y_u is the quantum yield of the sample to be tested; Y_s is the quantum yield of rhodamine B; F_u and F_s are the emission band area of the tested substance and dilute rhodamine B solution; A_u and A_s are the maximum absorbance values of the tested substance and dilute rhodamine B solution (the maximum absorbance values in the range of 0.01-0.05)

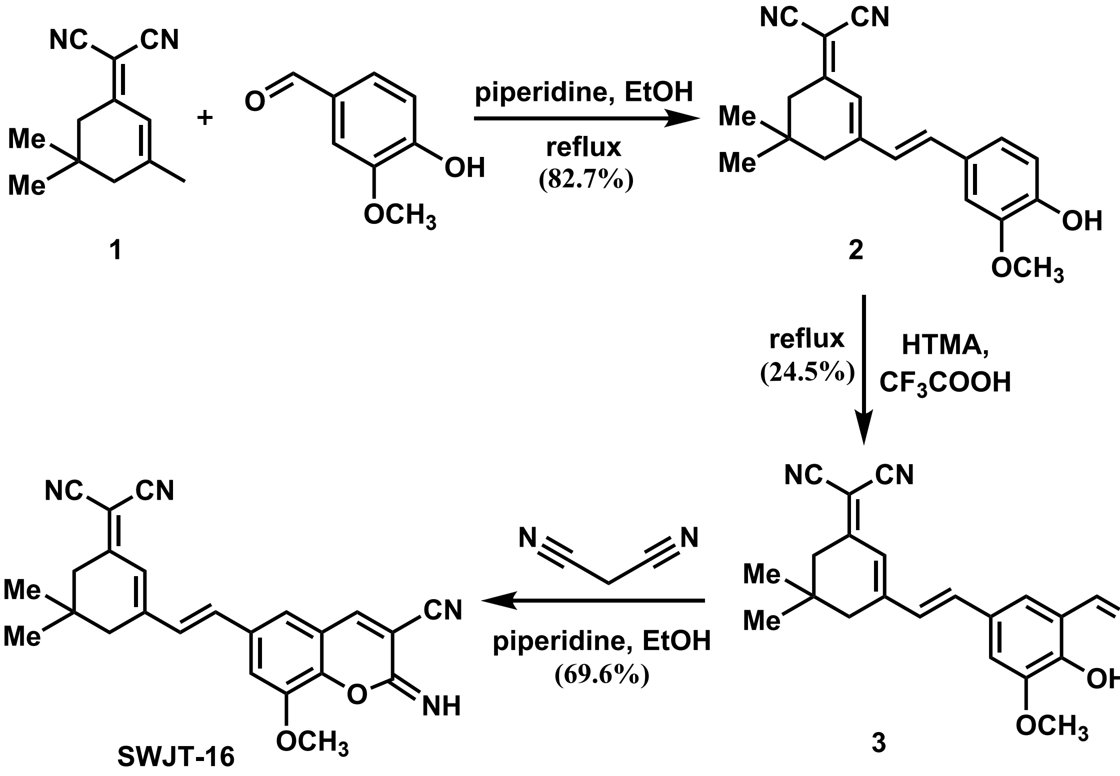
2.4 Response time test method for SWJT-16 to DCP

Because **SWJT-16** (10.0 μM) responded too quickly to DCP, the color change was observed immediately after the addition of DCP (50.0 μM), the fluorescence was scanned every 0.01 minute with a fluorescence spectrometer to collect emission peaks in the 490-800 nm range, and selected the emission peak at 554 nm for a time curve.

2.5 The fabrication of paper sensors

First, the probe **SWJT-16** (10.0 μM) was dissolved in DMF. The filter paper soaked in the solution containing **SWJT-16**. Then, the filter paper dried after 12 hours to get the test paper sensor. After adding different concentrations of DCP, the color change was observed within 1 minute, and then took pictures under visible light and ultraviolet light to take photos.

3. Synthesis of SWJT-16.



Scheme S1. Synthesis of **SWJT-16**.

4. ^{1}H, ^{13}C NMR spectra, LC-MS and HR-ESI-MS of SWJT-16.

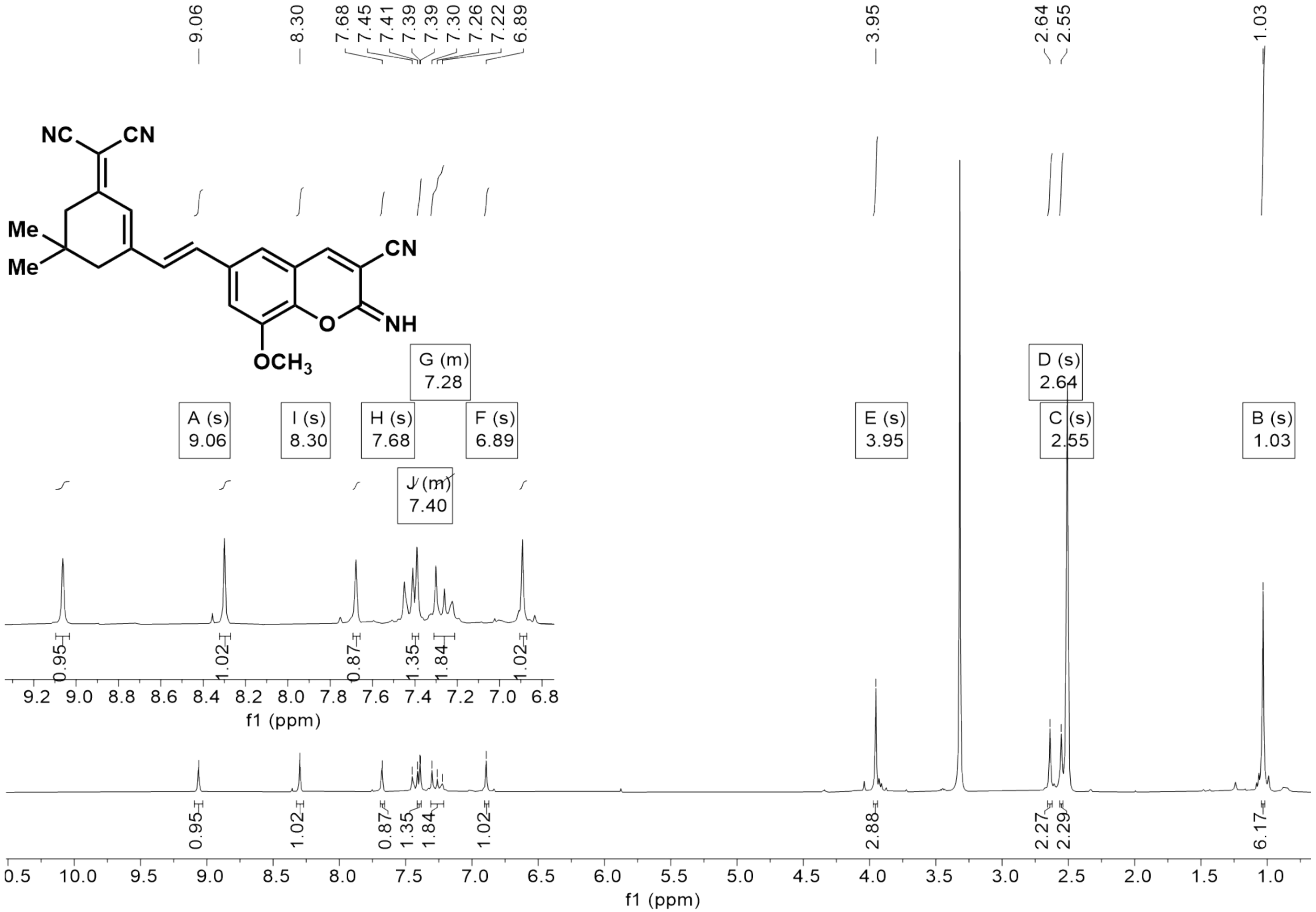


Fig. S1. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **SWJT-16**.

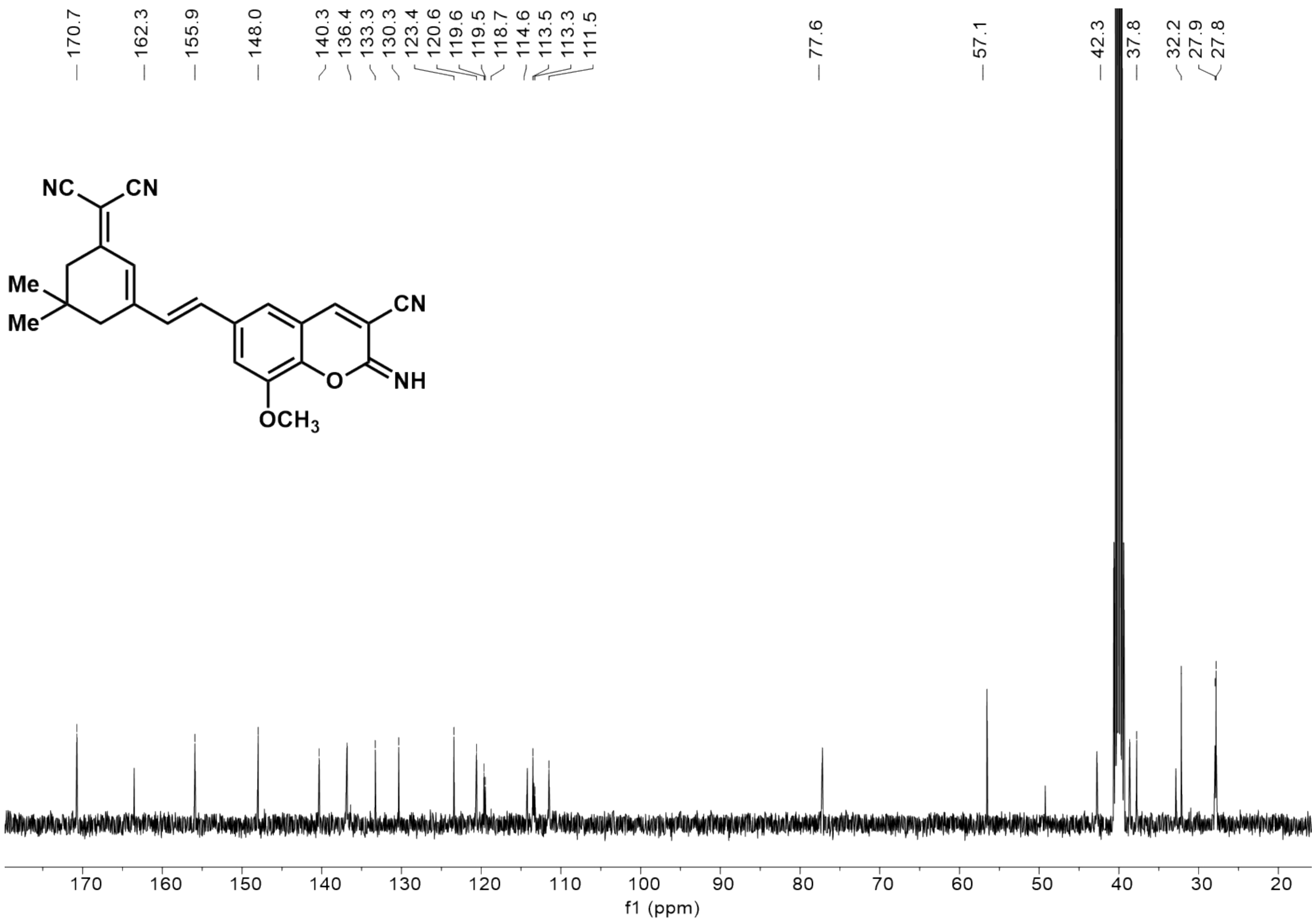


Fig. S2. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **SWJT-16**.

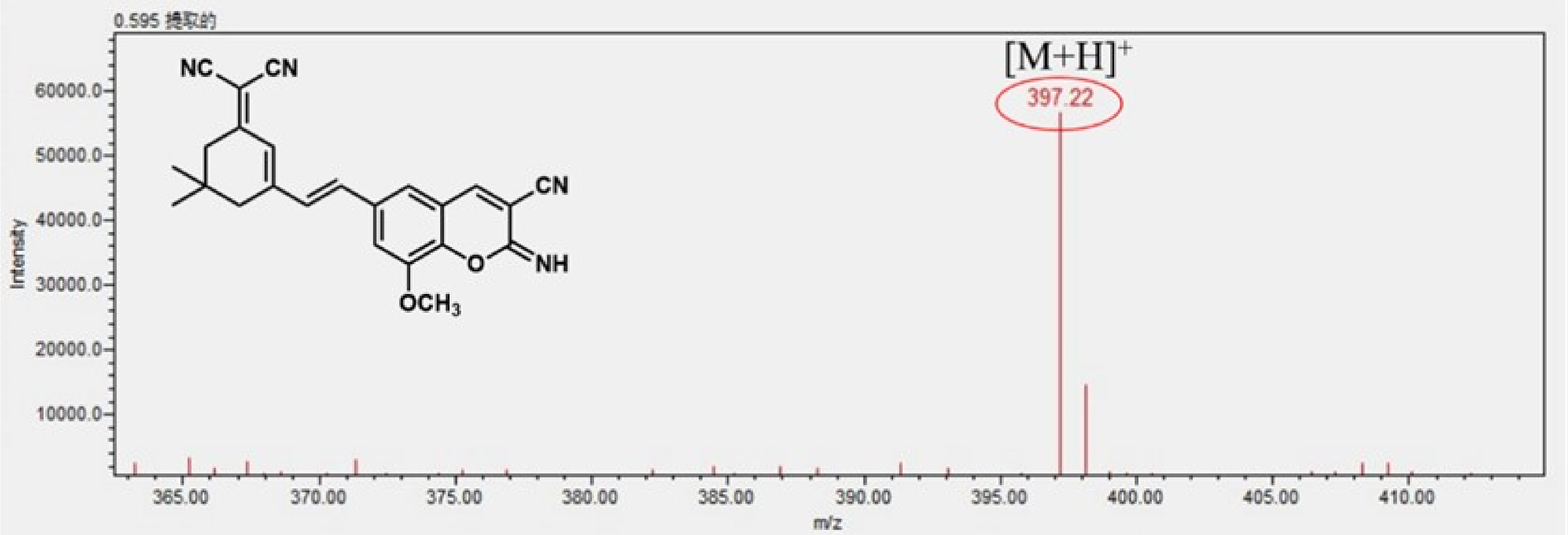


Fig. S3. LC-MS spectrum of **SWJT-16**.

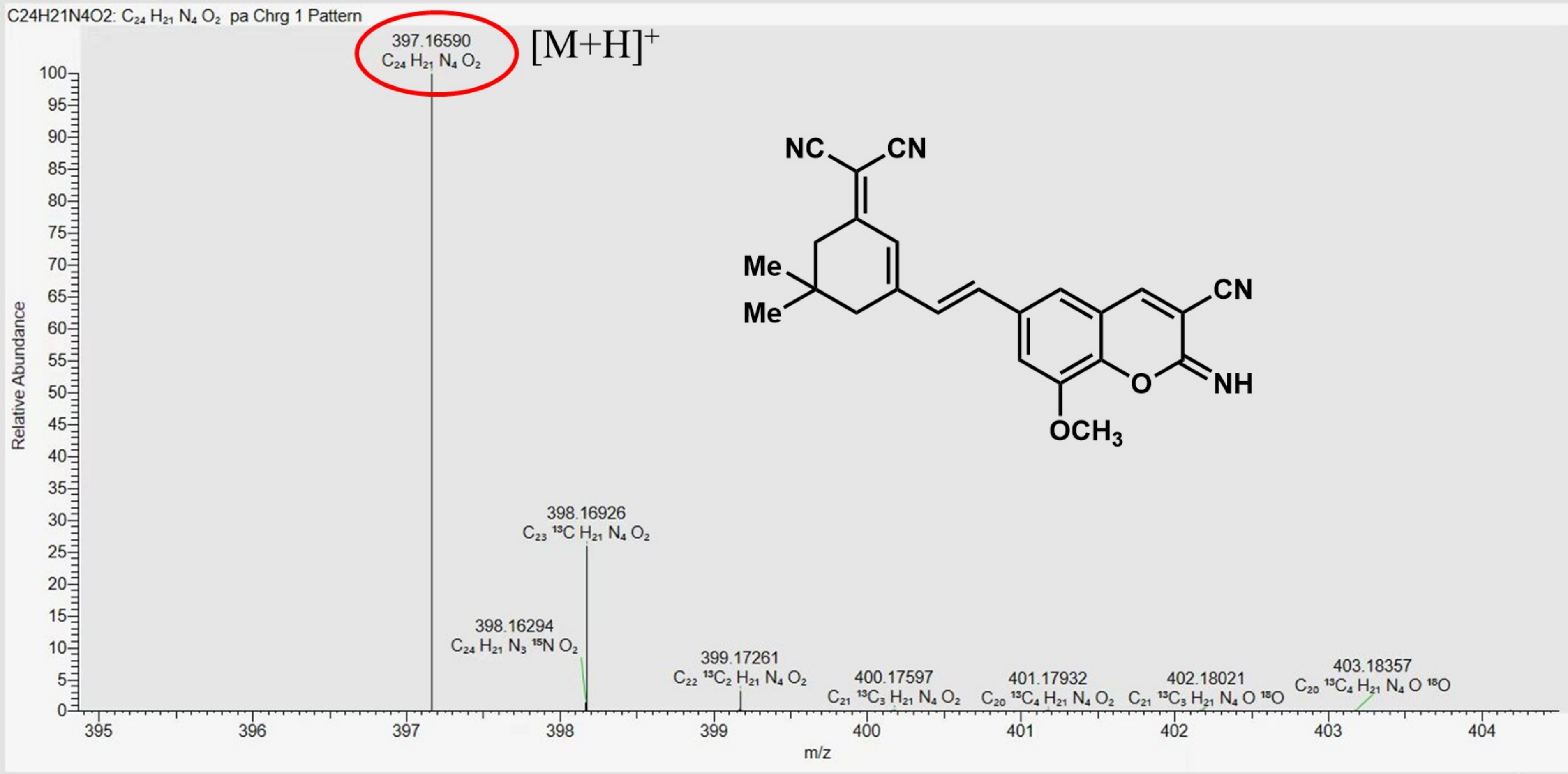


Fig. S4. HRMS spectrum of **SWJT-16**.

5. Solvent screening of SWJT-16.

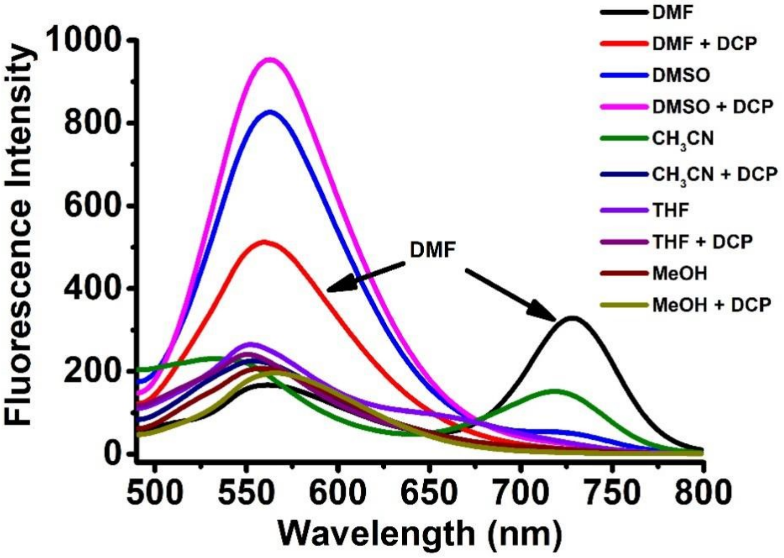


Fig. S5. The fluorescence emission spectra of **SWJT-16** (10.0 μM) and **SWJT-16** + DCP (50 μM) in different organic solvents (λ_{ex} = 470 nm).

6. The linear relationship of concentration titration.

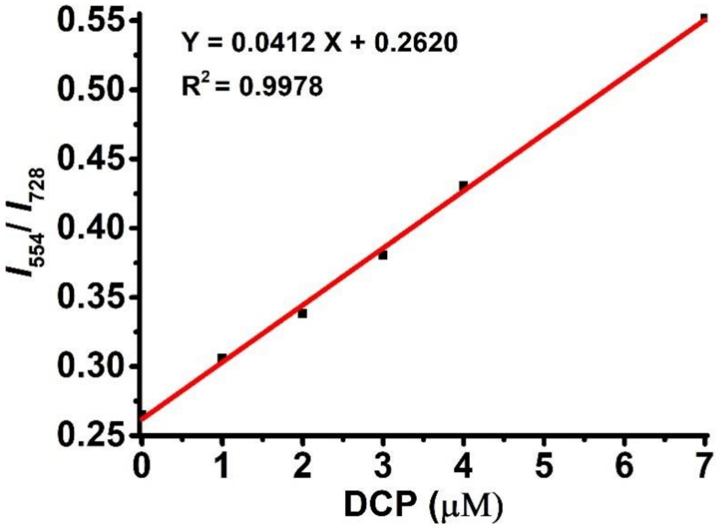


Fig. S6. Linear relationship between ratio at I_{554}/I_{728} and the concentration of DCP from 0 to 7.0 μM in DMF (λ_{ex} = 470 nm).

The detection limit (LOD) is calculated according to the following formula combined concentration titration linear equation.

LOD = K × δ / S Linear Equation：Y = 0.0412 X + 0.2620

K =3 δ = 0.0307(The standard deviation of the blank solution) S = 0.0412(The slope of the concentration titration curve)

LOD = 2.2 μM

7. The pseudo-first-order kinetics equation of SWJT-16.

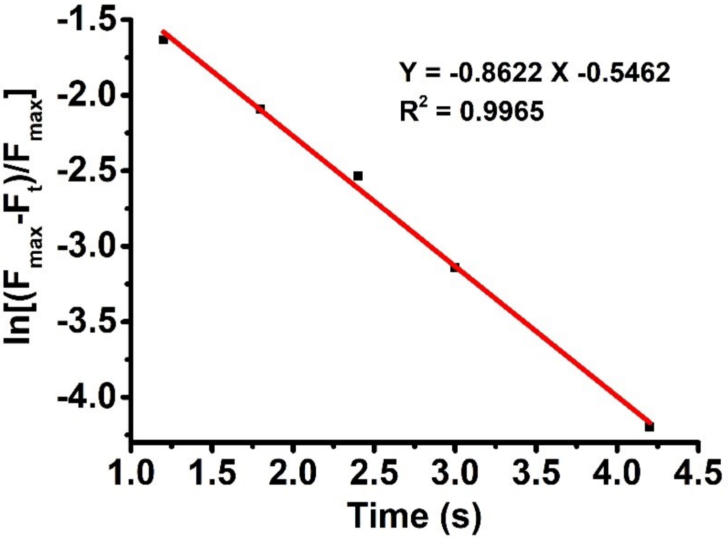


Fig. S7. The pseudo-first-order kinetics equation of **SWJT-16** (10.0 μM, λ_{ex} = 470 nm) with DCP (50.0 μM) in DMF.

The first-order reaction rate equation is as follows:

$$\ln[(F_{max}-F_t)/(F_{max})] = -k_{obs}\,t$$

$$t_{1/2} = \ln 2/k_{obs}$$

Where F_{max} and F_t are the fluorescence intensity at maximum emission and time t. k_{obs} is the pseudo-first-order rate constant.

$k_{obs} = 0.8622\ s^{-1}$

$t_{1/2} = 0.804$ s

8. Selectivity and competitiveness of probe SWJT-16.

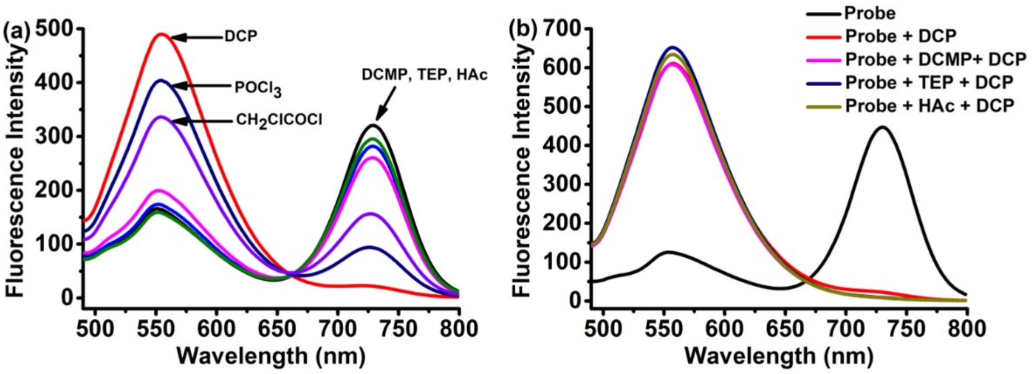


Fig. S8. (a) The fluorescence responses of selectivity studies of **SWJT-16** (10.0 μM) for various analytes (50.0 μM,) in DMF (λ_{ex} = 470 nm). (b) **SWJT-16** (10.0 μM) with various analytes and DCP in DMF (λ_{ex} = 470 nm).

9. LC-MS spectrum of SWJT-16 + DCP.

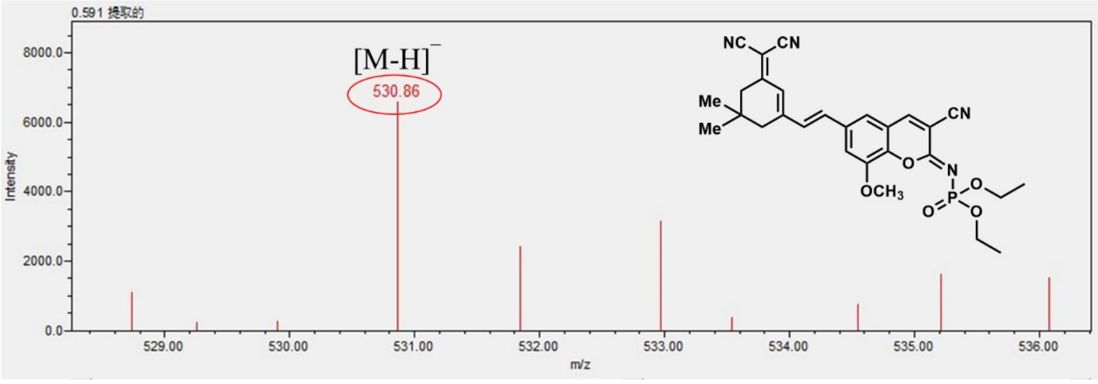


Fig. S9. LC-MS spectrum of **SWJT-16** + DCP

10. ^{31}P NMR spectra of compound 4 and DCP.

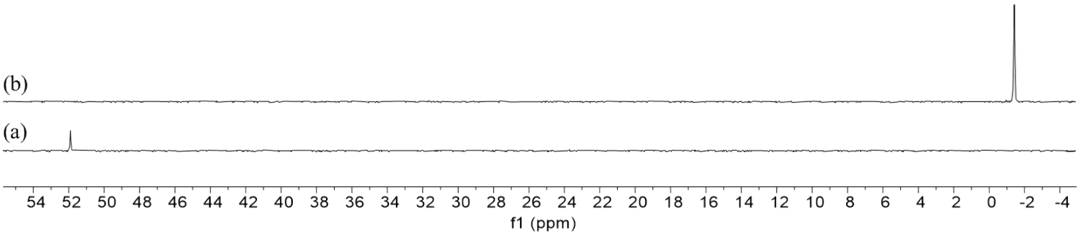


Fig. S10. ^{31}P NMR spectrum (162 MHz, DMSO-d_6) of (a) compound **4** and (b) DCP.

11. Energy distribution of SWJT-16 and compound 4.

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs	Minor contribs
1	23530.58144	424.97887379	1.1244	Singlet-A	HOMO->LUMO (96%)	H-1->LUMO (3%)
2	24421.83024	409.469720399	0.1016	Singlet-A	HOMO->L+1 (92%)	H-2->LUMO (2%), H-1->LUMO (3%)
3	27665.81456	361.456915657	0.1044	Singlet-A	H-2->LUMO (60%), H-1->LUMO (33%)	HOMO->L+1 (5%)
4	29160.37024	342.931173977	0.573	Singlet-A	H-2->LUMO (32%), H-1->LUMO (49%)	H-1->L+1 (9%), HOMO->LUMO (4%), HOMO->L+2 (3%)
5	31240.48848	320.097427619	0.0195	Singlet-A	H-2->L+1 (46%), H-1->L+1 (49%)	
6	32259.98032	309.981590218	0.0878	Singlet-A	H-2->L+1 (42%), H-1->L+1 (34%), HOMO->L+2 (12%)	H-3->LUMO (4%), H-1->LUMO (5%)
7	35289.41968	283.37105259	0.0259	Singlet-A	H-3->LUMO (61%), HOMO->L+2 (21%)	H-2->L+1 (5%), H-1->L+1 (3%), H-1->L+2 (3%)
8	36810.59184	271.66094051	0.0007	Singlet-A	H-4->LUMO (19%), H-4->L+1 (80%)	

Fig. S11. Energy distribution of **SWJT-16.**

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs	Minor contribs
1	23415.24336	427.072221555	0.6921	Singlet-A	HOMO->LUMO (47%), HOMO->L+1 (49%)	H-1->LUMO (3%)
2	24194.38032	413.319120711	0.6494	Singlet-A	HOMO->LUMO (48%), HOMO->L+1 (46%)	H-2->LUMO (4%)
3	27917.46128	358.19875954	0.0219	Singlet-A	H-2->LUMO (46%), H-1->LUMO (47%)	HOMO->L+1 (2%)
4	29048.2584	344.254717866	0.4984	Singlet-A	H-2->LUMO (42%), H-1->LUMO (27%), H-1->L+1 (16%)	H-2->L+1 (6%), HOMO->LUMO (3%), HOMO->L+2 (2%)
5	29512.83696	338.835606131	0.0343	Singlet-A	H-3->L+1 (27%), H-1->L+1 (44%)	H-4->L+1 (8%), H-3->LUMO (3%), H-2->LUMO (4%), H-1->LUMO (9%)
6	30252.45248	330.55171334	0.0016	Singlet-A	H-3->L+1 (21%), H-2->L+1 (38%), H-1->L+1 (21%)	H-4->L+1 (5%), H-3->LUMO (8%)
7	31136.44224	321.167072427	0.0035	Singlet-A	H-3->LUMO (82%)	H-4->LUMO (3%), H-4->L+1 (2%), H-3->L+1 (6%), H-2->L+1 (3%)
8	31405.02672	318.420362739	0.1157	Singlet-A	H-3->L+1 (20%), H-2->L+1 (41%), H-1->L+1 (12%)	H-5->L+1 (3%), H-4->L+1 (3%), H-1->LUMO (7%), HOMO->L+2 (7%)

Fig. S12. Energy distribution of compound **4**