Electronic Supplementary Information

A simple but effective fluorescent probe for the detection of bisulfite

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Tel: 0086-538-6236195.
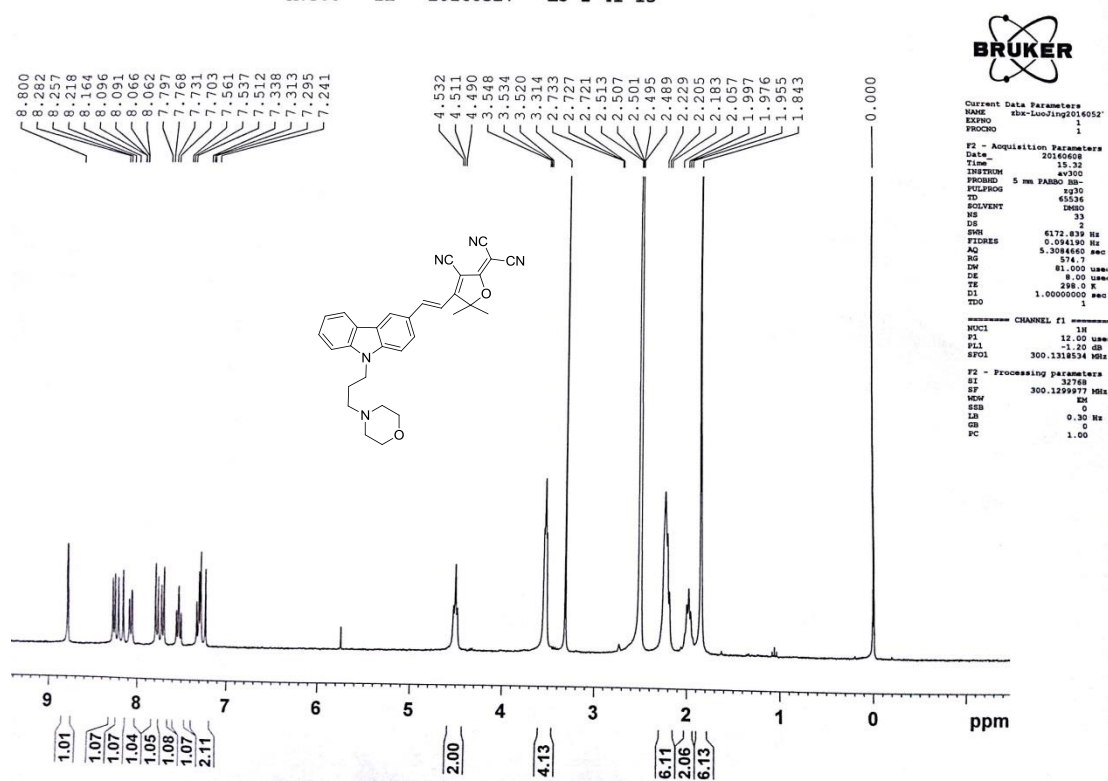
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Calculation of the detection limit (LOD)

$$LOD = 3\sigma/k$$

Where, σ is the standard deviation of the blank solution and k is the slope of the linear calibration plot between the fluorescence emission intensity and the concentration of hypochlorite.

The concentration of PML and HSO_3^- were the same and we used the formula to calculate the rate constant. Formula: $dx/dt=k(c-x)^2$, x is the concentration of the reactants consumed when the time was t, c is the initial concentration, k is the rate constant. Integral to get a new formula $x/c(c-x)= kt$. We measured the fluorescence intensity and the fluorescence intensity is proportional to the concentration. Therefore, as long as measured by the experiment of when the value of x at different time t, it is a straight line which proved that it is a second-order reaction. The rate constant k can be calculated from formula. $k = 1.457 \times 10^5 \, M^{-1} min^{-1}$.

Fig. S1 ^{1}H NMR spectrum of probe **PML** (DMSO-d_6).

Fig. S2 ^{13}C NMR spectrum of probe **PML** (DMSO-d_6).

+ESI Scan (1.037 min) Frag=135.0V LJ—1-41-13.d Subtract

×10 5

504.2339

526.2147

Counts vs. Mass-to-Charge (m/z)

Fig. S3 MS spectrum of probe **PML**.

Transmittance [%]

3446.78

2929.45
2862.98
2818.83
2775.12

2226.63

1631.55
1555.00

1375.92
1296.76
1211.06
1140.33

964.90

755.09

526.33

Wavenumber cm-1
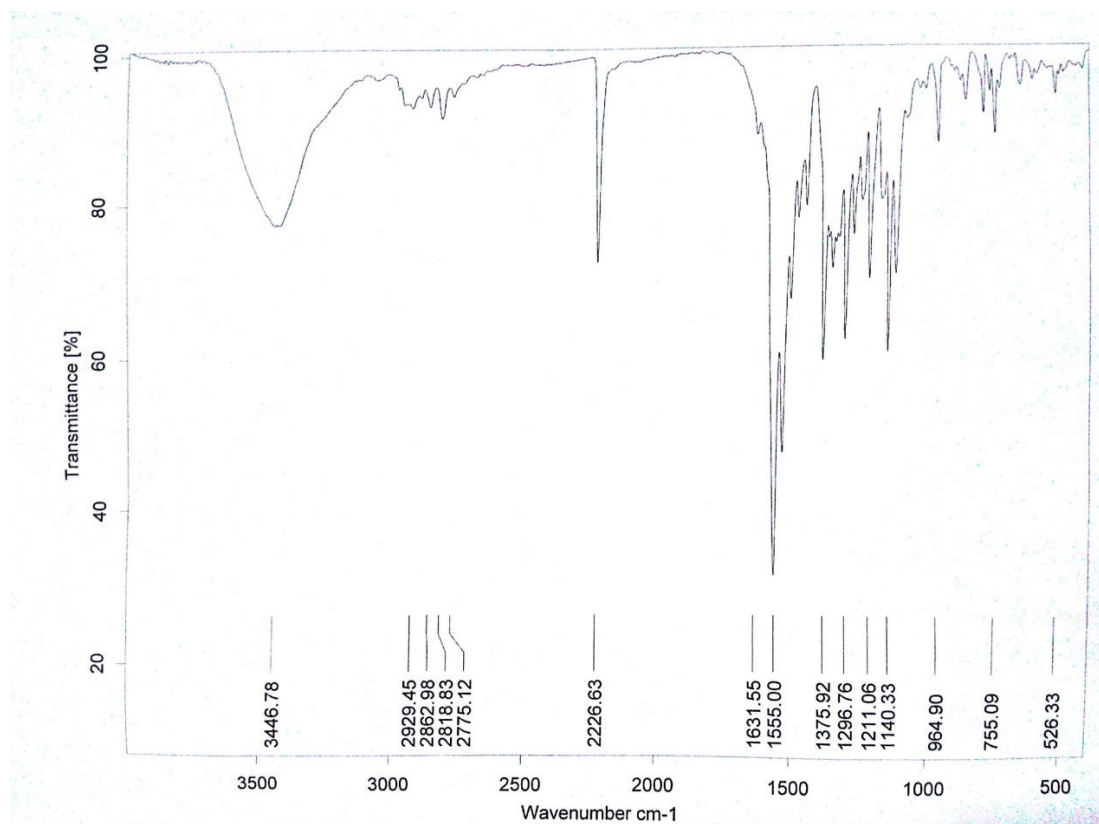
Fig. S4 IR spectrum of probe **PML**.

10.073

8.776
8.327
8.302
8.036
8.031
8.008
8.003
7.819
7.791
7.740
7.713
7.593
7.591
7.567
7.542
7.355
7.330
7.306

4.621
4.598
4.575
3.686
3.665
3.643
3.331
2.518
2.512
2.506
2.500
2.494
2.302
2.280
2.257
2.235
2.213

-0.000

BRUKER

Current Data Parameters
NAME   zbx-LuoJing20160516
EXPNO   1
PROCNO   1

F2 - Acquisition Parameters
Date_   20160528
Time   12.49
INSTRUM   av300
PROBHD   5 mm PABBO BB-
PULPROG   zg30
TD   65536
SOLVENT   DMSO
NS   64
DS   2
SWH   6172.839 Hz
FIDRES   0.094190 Hz
AQ   5.3084660 sec
RG   456.1
DW   81.000 us
DE   8.00 us
TE   673.2 K
D1   1.00000000 sec
TD0   1

======= CHANNEL f1 =======
NUC1   1H
P1   12.00 us
PL1   -1.20 dB
SFO1   300.1318534 MHz

F2 - Processing parameters
SI   32768
SF   300.1299959 MHz
WDW   EM
SSB   0
LB   0.30 Hz
GB   0
PC   1.00

Fig. S5 ^{1}H NMR spectrum of 9-(3-bromopropyl)-9H-carbazole-3-carbaldehyde.

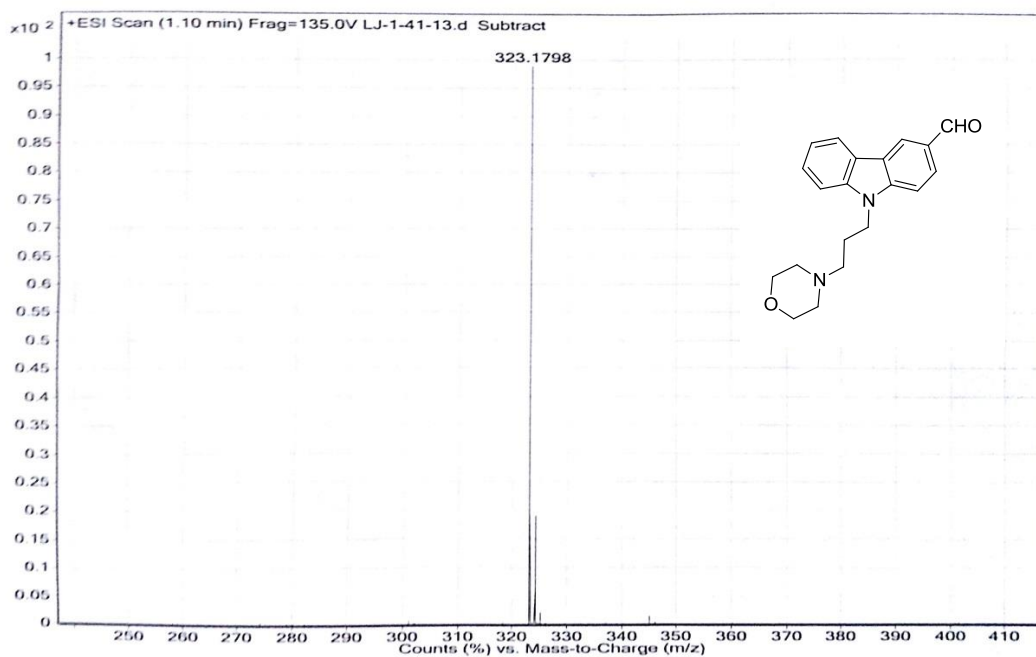x10 2   +ESI Scan (1.10 min) Frag=135.0V LJ-1-41-13.d Subtract

323.1798

Counts (%) vs. Mass-to-Charge (m/z)

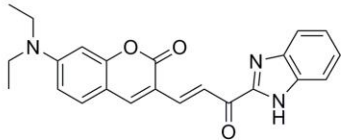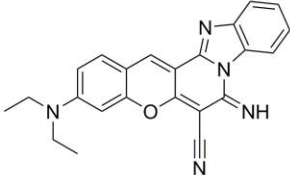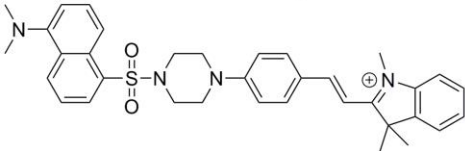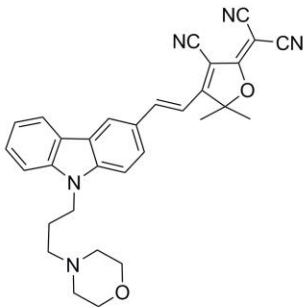**Fig. S6** MS spectrum of compound 4
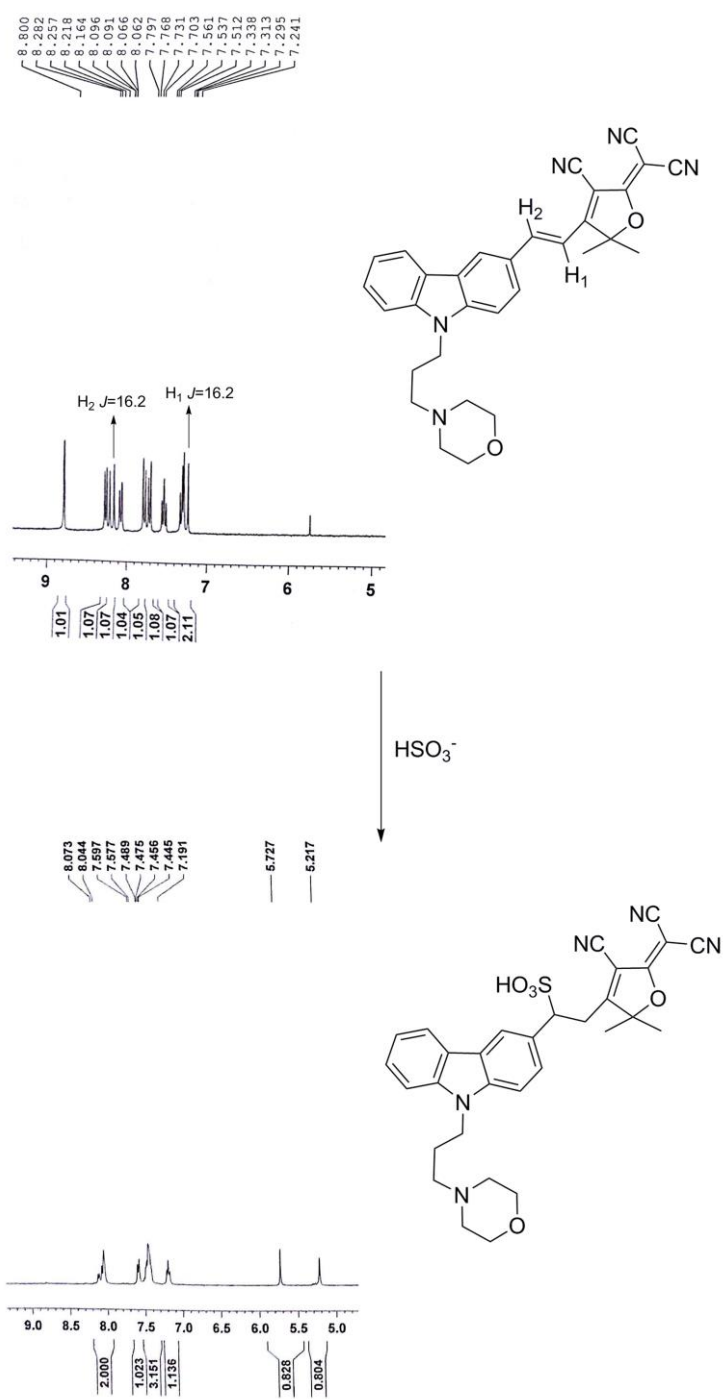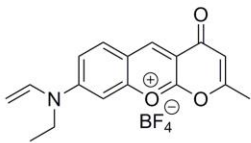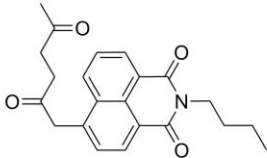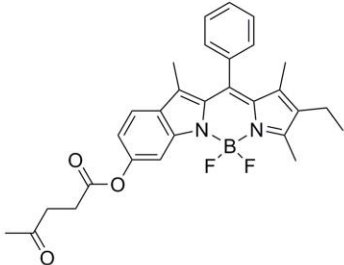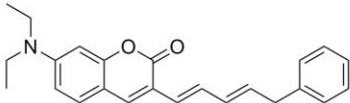
Fig. S7 ^{1}H NMR titration process of PML and HSO$_3$$^{-}$

Table. S1 Comparison of fluorescent probes for HSO_3^-/SO_3^{2-}.

Probe structures	LOD/ μ M	λ ex/nm	λ em/nm	Response time	Ref.
	0.61	465 nm	510/560 nm	5 min	1
	1.57	380 nm	414/554 nm	60 min	2
	58	538 nm	570/647 nm	5 min	3
	0.23	425 nm	488/630 nm	30 min	4
	0.058	415 nm	458/605 nm	60 min	5
	1.76	340 nm	575 nm	2 min	6
	0.1	410 nm	530/582 nm	2 min	7
	2.08	515 nm	618 nm	10 min	This work

Reference:

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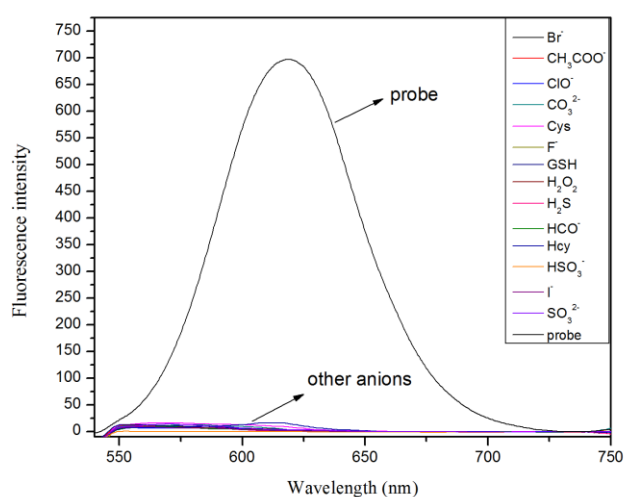
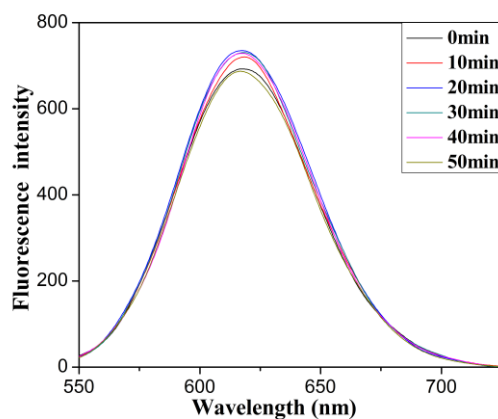**Fig. S8** Fluorescence responses of probe **PML** (5 μM) toward HSO_3^- (18 eq.) with different anions.

Fig. S9 The stability of fluorescence probe **PML**.