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Electronic Supplementary Information

A reversible near-infrared fluorescence probe for the monitoring HSO_3^-/H_2O_2 regulated cycles *in vivo*

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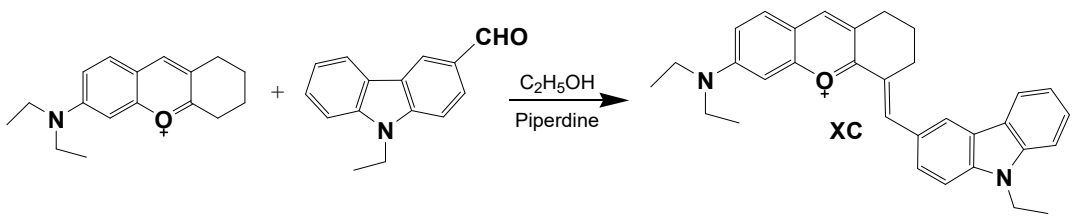

Scheme S1 Synthetic procedure of the near-infrared out fluorescent probe (**XC**).

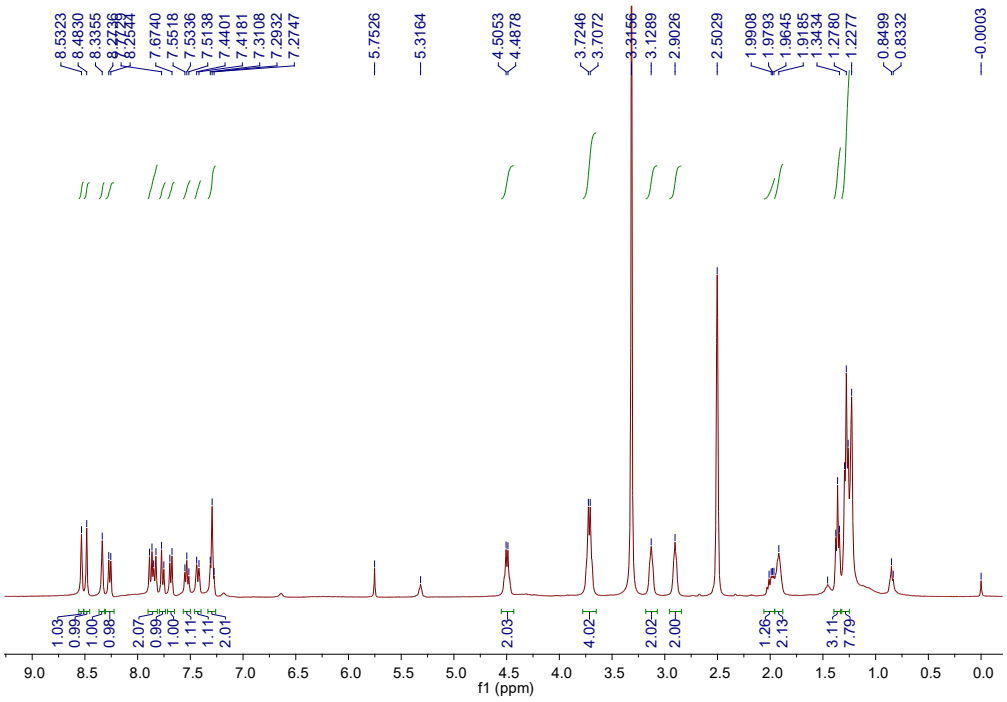

Fig. S1 ^{1}H NMR of **XC** (DMSO-d_6).

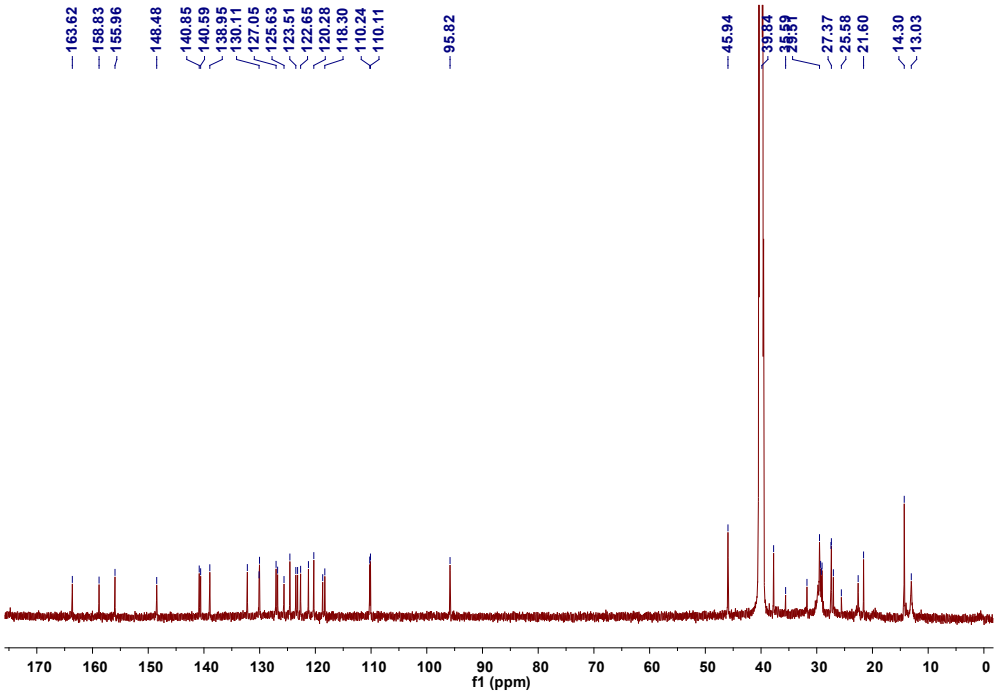

Fig. S2 ^{13}C NMR of **XC** (DMSO-d_6).

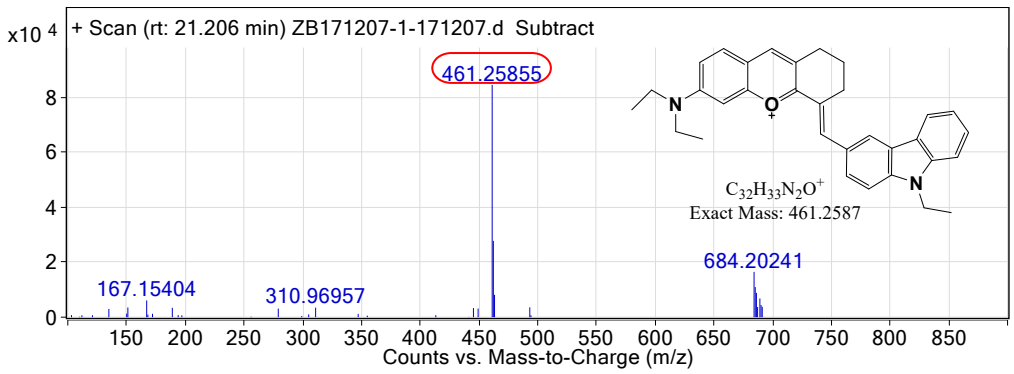

Fig. S3 HR MS of **XC**.

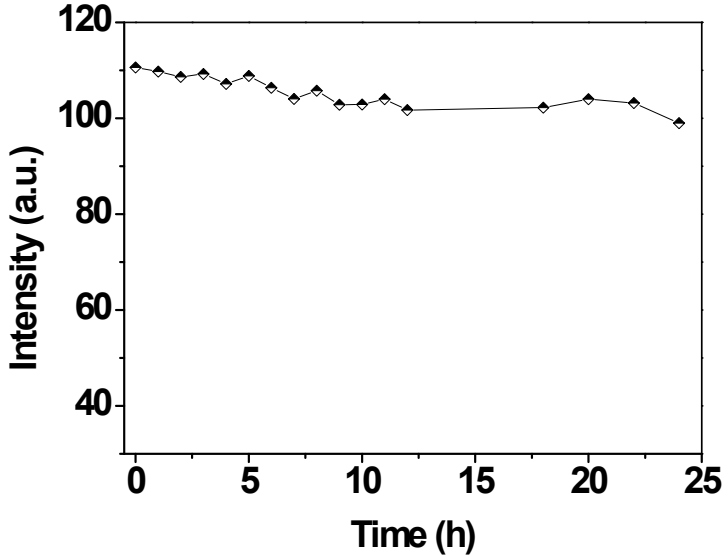

Fig. S4 Fluorescence intensities of **XC** (10 μM) at different time in PBS buffer (DMSO:HEPES=3:7, v/v; pH=7.4). The intensities were recorded at 684 nm, excitation was performed at 605 nm.

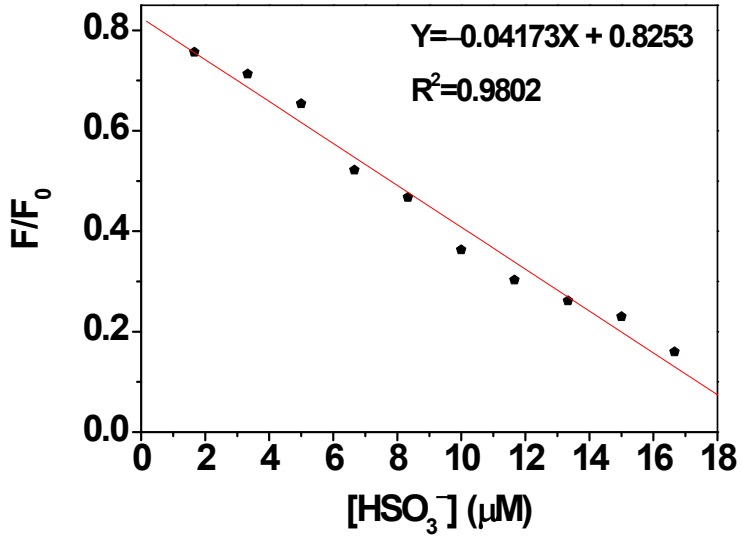

Fig. S5 The fluorescence intensity changes at 684 nm of **XC** (5 μM) as a function of HSO_3^- concentration (1.66-16.66 μM). Excitation was performed at 605 nm.

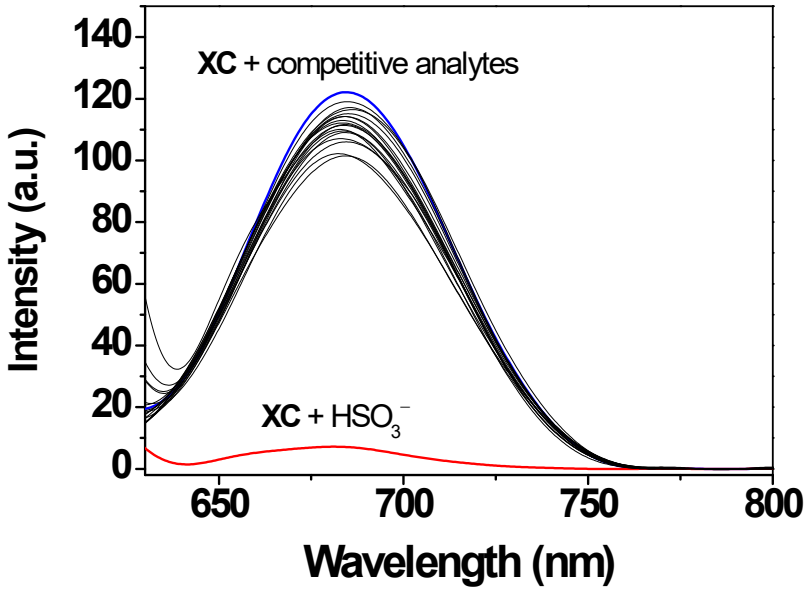

Fig. S6 Fluorescence spectra of **XC** (10 μM) in the presence of various analytes (50 μM) in HEPES aqueous buffer (DMSO:HEPES=3:7, 20 mM, pH=7.4). Excitation was performed at 605nm.

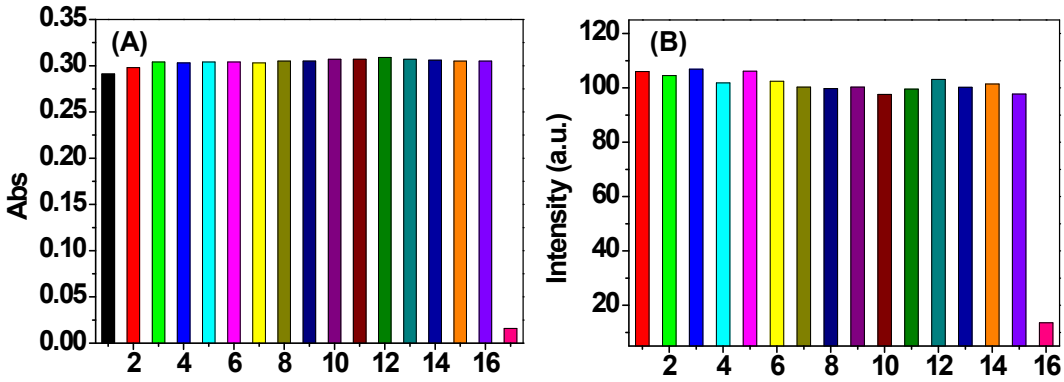

Fig. S7 (A) Absorption spectra and (B) fluorescence response of **XC** (10 μM) towards various biological cations (40 μM) in PBS buffer (DMSO:HEPES=3:7, v/v; pH=7.4): 1. Blank, 2. Zn^{2+}, 3. Ni^{2+}, 4. Al^{3+}, 5. Cr^{3+}, 6. Ca^{2+}, 7. Mg^{2+}, 8. Ba^{2+}, 9. Li^{+}, 10. K^{+}, 11. Fe^{3+}, 12. Co^{2+}, 13. Cd^{2+}, 14. Pb^{2+}, 15. Na^{+}, 16. HSO_3^{-}. The fluorescence intensities were recorded at 684 nm, excitation at 605 nm.

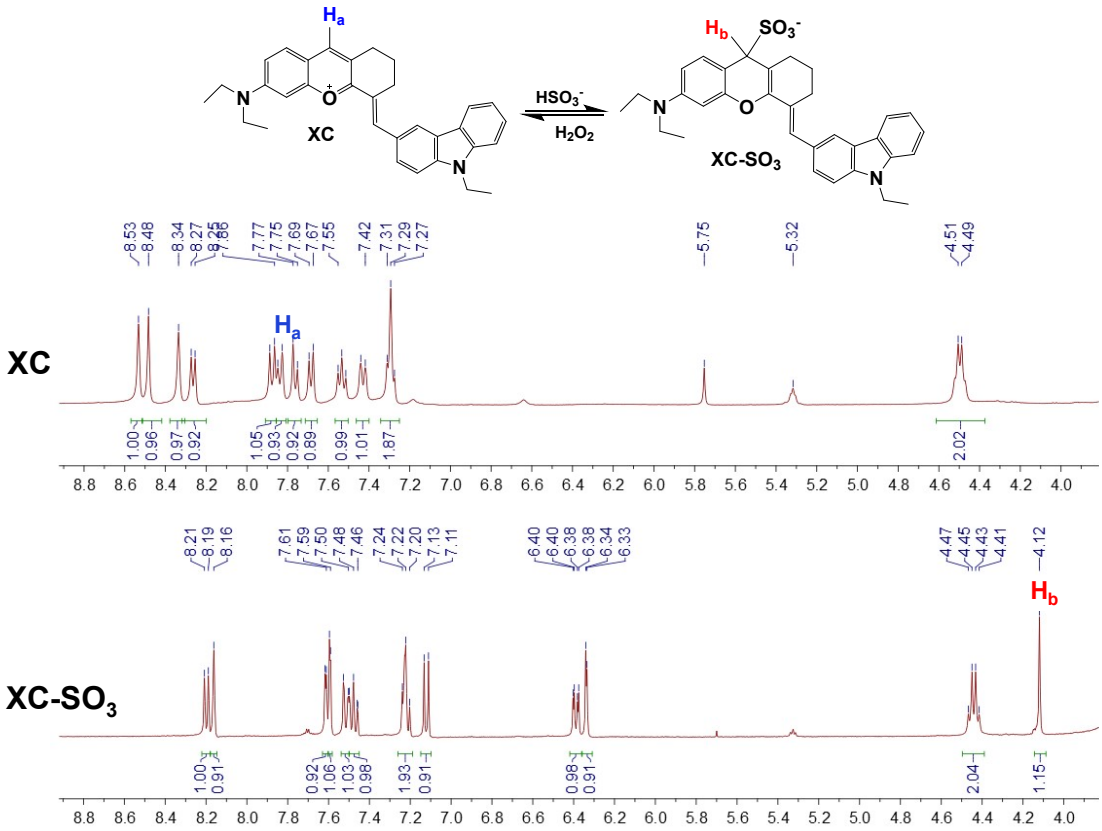

Fig. S8 ^{1}H NMR of **XC** in the presence of HSO_3^- in DMSO-d_6/D_2O mixed solvent.

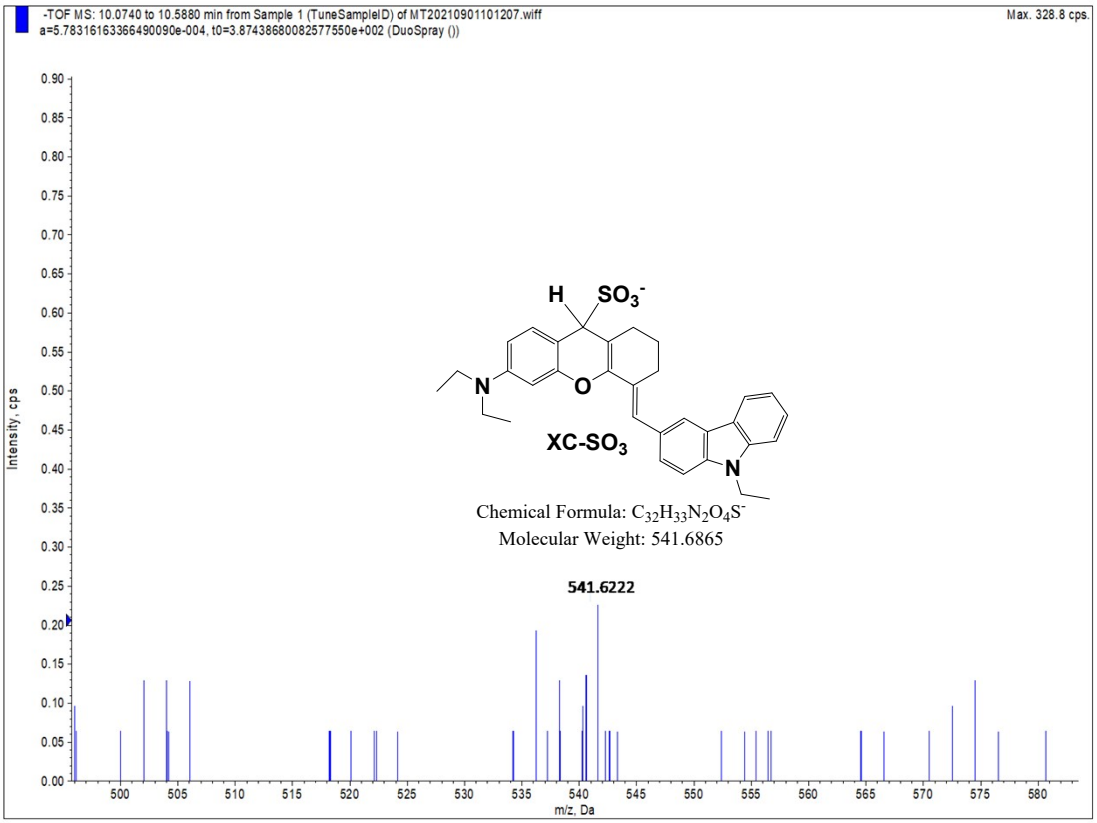

Fig. S9 HR MS of **XC** in the presence of HSO_3^-.

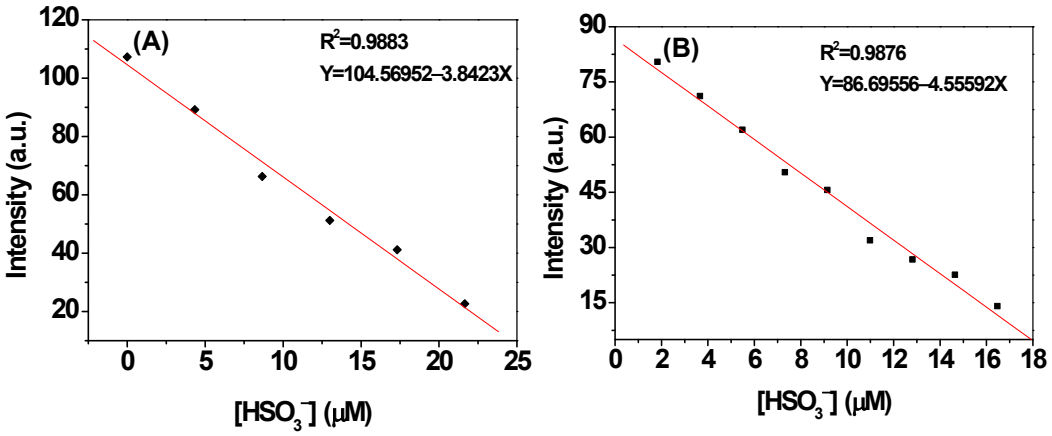

Fig. S10 The fluorescence intensity changes at 684 nm of **XC** (5 μM) as a function of HSO_3^- concentration in the aqueous solution of (A) white wine and (B) sugar samples. Excitation was performed at 605 nm.

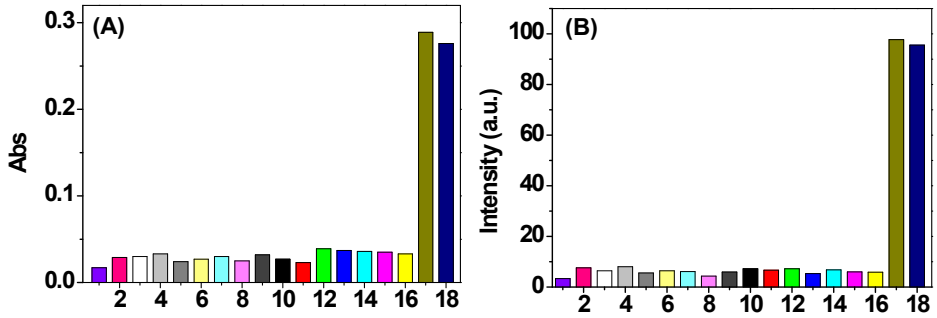

Fig. S11 (A) Absorption and (B) fluorescence spectra response of **XC-SO$_3$** (10 μM) towards various biological cations (50 μM) in PBS buffer (DMSO:HEPES=3:7, v/v; pH=7.4): 1. Blank, 2. Zn^{2+}, 3. Ni^{2+}, 4. Al^{3+}, 5. Cr^{3+}, 6. Ca^{2+}, 7. Mg^{2+}, 8. Ba^{2+}, 9. Li^+, 10. K^+, 11. Fe^{3+}, 12. Co^{2+}, 13. Cd^{2+}, 14. Pb^{2+}, 15. Na^+, 16. mixed cations, 17. HSO_3^-, 18. mixed cations + HSO_3^-. The fluorescence intensities were recorded at 684 nm, excitation at 605 nm.

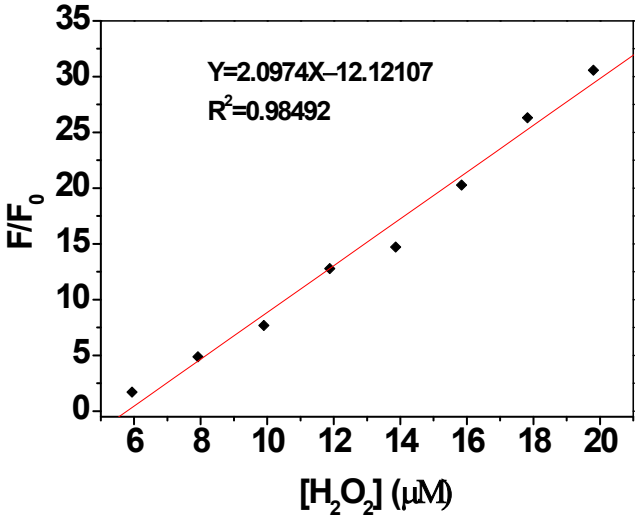

Fig. S12 Fluorescence spectra of **XC-SO$_3$** (5 μM) in the presence of different amounts of H_2O_2 (6-20 μM) in HEPES aqueous buffer (DMSO: HEPES=3:7, 20 mM, pH=7.4). The intensities were recorded at 684 nm, excitation was performed at 605 nm.

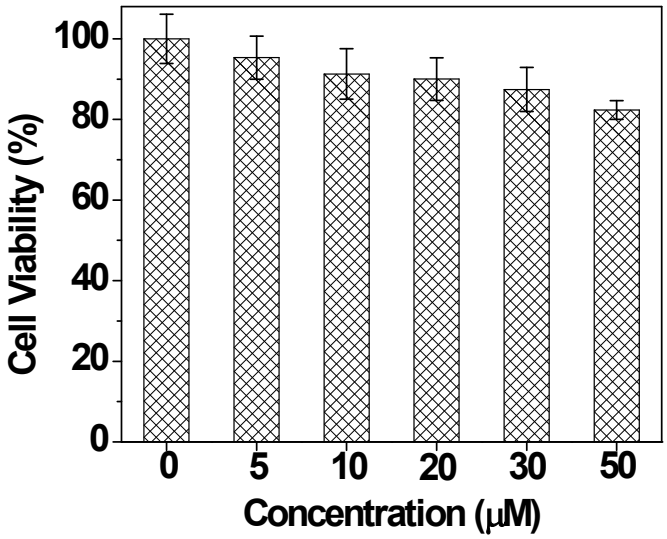

Fig. S13 The viability of HeLa cells incubated with different concentrations of **XC** (0-50 μM) for 24 h.

Table S1. Comparison of this work with reported fluorescent probes for HSO_3^- detection.

Probes	Near-infrared	Reversible response	Selectivity	Detection limit	Response time	Detection of HSO_3^- intake in live animals	Detection of HSO_3^- in food samples	Test papers	Ref.
ASHTI	619nm	No	HSO_3^-	0.27 μM	8min	No	No	Yes	1
QPCT	537nm/590 nm	No	HSO_3^-	0.44 μM	7min	No	No	No	2
CPC	470nm/627nm	No	HSO_3^-/ SO_3^{2-}	18 nM	10min	No	No	No	3
PCPT	568nm/648nm	No	HSO_3^-/ SO_3^{2-}	80.5 nM	15min	No	No	No	4
NBIS	534nm/610 nm	No	HSO_3^-/ SO_3^{2-}	16.2 nM	12min	No	No	No	5
Probe 1	445nm/570 nm	No	HSO_3^-	1.29 μmol/L	2min	No	No	No	6

Cy-p-Np	527nm/590 nm	No	HSO_3^-	98.1 nM	2.5min	No	No	No	7
BCVTI	608nm	No	HSO_3^-	3.3 nM	4min	No	Yes	No	8
HDI	460nm/565 nm	No	HSO_3^-/ SO_3^{2-}	80 nM	2min	No	No	No	9
DQ	620nm	No	HSO_3^-	0.11 μM	15s	No	Yes	Yes	10
TFBN	504nm/644 nm	No	HSO_3^-/ SO_3^{2-}	39 nM	3min	Yes	No	No	11
CM−BA	462nm/568 nm	No	HSO_3^-/ SO_3^{2-}	105 nM	20s	Yes	Yes	Yes	12
KQ−SO2	475nm/600 nm	No	HSO_3^-	10.28 nM	1min	Yes	Yes	Yes	13
CMQ	640nm	No	HSO_3^-	15.6 nM	5s	Yes	Yes	No	14
probe 1	450nm/594 nm	No	HSO_3^-	3.21 μM	2.5min	No	Yes	No	15
Ph-CN	460nm/660 nm	No	HSO_3^-	0.16 μM	5s	Yes	No	No	16
probe 1	514nm	No	HSO_3^-	22.8 nM	10s	No	No	No	17
Ru-azo	635nm	No	HSO_3^-	0.69 μM	60min	No	Yes	No	18
Q5	485nm/650 nm	No	HSO_3^-	89 nM	30min	No	No	No	19
BQDs	595nm/518 nm	No	HSO_3^-	0.5 μM	10min	No	No	No	20
SNB	478nm/671 nm	No	HSO_3^-/ SO_3^{2-}	17 nM	50min	No	No	No	21
DCQN	660nm	No	HSO_3^-	24 nM	6s	Yes	No	No	22
HEM-CO-Ph	615nm	No	HSO_3^-/ SO_3^{2-}	137 nM	5min	No	No	No	23

ZACA	490nm/620 nm	No	HSO_3^-/ SO_3^{2-}	15.6 nM	13min	No	No	No	24
Mito-HN	520nm/668 nm	No	HSO_3^-/ SO_3^{2-}	0.17 μM	30s	Yes	No	No	25
MITO-TPE	455nm	No	HSO_3^-	27.22 μM	20s	Yes	No	No	26
Hcy-Mo	596nm	No	HSO_3^-	80 nM	30s	Yes	No	Yes	27
RBC	456nm/583 nm	No	HSO_3^-/ SO_3^{2-}	6.6×10^{-8} M	35s	No	No	Yes	28
TBQN	514nm	No	HSO_3^-	3.19×10^{-8} M	3min	No	No	No	29
XC	605nm/684 nm	HSO_3^-/H_2O_2	HSO_3^-	1.02μM	within 5 seconds	Yes	Yes	Yes	**This work**

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Table S2. Comparison of this work with reported fluorescent probes for H_2O_2 detection.

Probes	Near-infrared	Reversible response	Selectivity	Detection limit	Response time	Ref.
BOD-H_2O_2	725nm	No	H_2O_2	4.3×10^{-7} mol/L	-	1
XH-2	638 nm	No	H_2O_2	91 nM	40min	2
BT-HP	550nm	No	H_2O_2	1.5×10^{-7} M	120s	3
Cy-H_2O_2	790 nm	No	H_2O_2	65 nM	10min	4

DCHP	653nm	No	H_2O_2	5.3 μM	15min	5
Cou-CHO	502nm	No	H_2O_2	31 nM	20min	6
RhB-NIR	730nm	No	H_2O_2	61 nM	10min	7
GCP	482nm/706nm	No	H_2O_2	0.33 μM	15min	8
BPN-TOB	471nm	No	H_2O_2	67 nM	10min	9
Hcy-OB	HSO_3^-:392nm H_2O_2:520nm	No	HSO_3^-/H_2O_2	HSO_3^-:120 nM H_2O_2:70 nM	HSO_3^-:1min H_2O_2:20min	10
BTFMB	542nm	No	H_2O_2	109 nM	45min	11
TPP-HCy-BOH and HCy-BOH	TPP-HCy-BOH:716nm HCy-BOH:706nm	No	H_2O_2	TPP-HCy-BOH:0.348 μM HCy-BOH:1.064 μM	-	12
QX-B	772nm	No	H_2O_2	0.17 μM	5min	13
GW-1	549nm	No	H_2O_2	-	30min	14
Mito-Bor	730nm	No	H_2O_2	23 nM	25min	15
TTPB	Viscosity：666nm H_2O_2：586nm	No	Viscosity/ H_2O_2	0.141 μmol/L	-	16
QVB-B	464nm/580nm	No	H_2O_2	-	60min	17
TC-H_2O_2	920nm	No	H_2O_2	-	30min	18
TTPy-H_2O_2	590nm	No	H_2O_2	0.25 μM	50min	19
NPT-H_2O_2	550nm/425nm	No	H_2O_2	12.8 nM	40s	20
XC-SO_3	605nm/684nm	HSO_3^-/H_2O_2	H_2O_2	0.84 μM	16 min	This work

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