Supporting Information for

Ultrasensitive Fluorescence Detection of Peroxymonosulfate Based on a Sulfate Radical-Mediated Aromatic Hydroxylation

Gui-Xiang Huang[†], Jin-Yan Si[†], Chen Qian, Wei-Kang Wang, Shu-Chuan Mei,

Chu-Ya Wang, Han-Qing Yu*

CAS Key Laboratory of Urban Pollutant Conversion, Department of Applied

Chemistry, University of Science & Technology of China, Hefei, 230026, China

[†] These authors contributed equally to this work.

*Corresponding author:

Prof. Han-Qing Yu, E-mail: hqyu@ustc.edu.cn

This supplementary material contains 15-page document, including 3 tables, 10 figures, references and this cover page.

method	linear range (µM)	detection limit (µM)	reference
thermometric titrimetry	unreported	50	1
HPLC	unreported	0.5	2
chemiluminescence	0.4-2	0.05	3
KI spectrophotometry	12-115	3.62	4
DPD spectrophotometry	10-100	10	5
MO spectrophotometry	0.2-100	0.09	6
AO7 spectrophotometry	0-80	0.08	7
MB spectrophotometry	0-100	0.10	7
MV spectrophotometry	0-80	0.08	7
RhB spectrophotometry	0-40	0.04	7
BA fluorometry	0-100	0.01	this work

Table S1. Comparison of Linear Range and Detection Limit between the BAFluorometry and Other PMS Determination Methods.

cation ^a	concentration (mg L ⁻¹)	anion ^b	concentration (mg L ⁻¹)
K^+	30	Cl ⁻	125
Ca ²⁺	80	HCO_{3}^{-}	200
Mg^{2+}	35	NO_3^-	6
Al ³⁺	0.1	SO_4^{2-}	100
Fe ³⁺	0.1	PO4 ³⁻	2.5
Mn^{2+}	0.05		

Table S2. Concentrations of the Tested Cations and Anions.

^aThe counter ion is SO_4^{2-} ; ^bthe counter ion is Na⁺.

$\Delta [\mathrm{HSO}_5^-]$ ($\mu \mathrm{M}$)	Δ[BA] (μM)	$\Delta[BA]/\Delta[HSO_5^-]$	Δ[SA] (μM)	$\Delta[SA]/\Delta[HSO_5^-]$
70	31.3	0.45	8.8	0.13
350	221.4	0.63	39.2	0.11
700	346.5	0.49	64.6	0.09
average	_	0.52	_	0.11

Table S3. Conversion Factor of BA and SA Based on the Activation of PMS in the BA/PMS/Co²⁺ System.

 Δ [SA]: the production of SA per unit volume

 $\Delta[\mathrm{HSO}_5^-]$ and $\Delta[\mathrm{BA}]$: the consumption of HSO_5^- and BA per unit volume

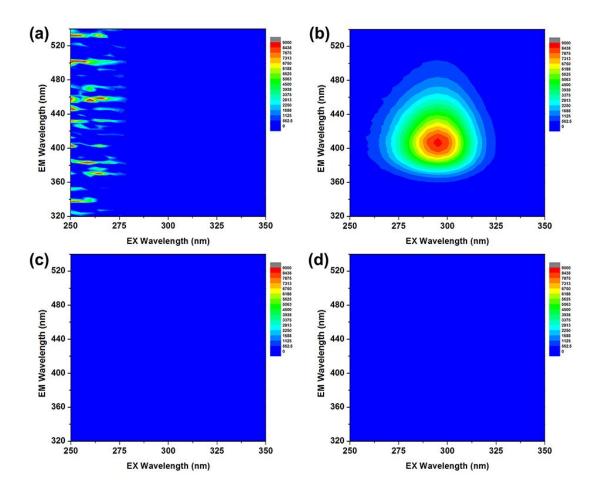


Figure S1. EEMS of BA (a), ortho- (b), meta- (c), and para- (d) hydroxybenzoic acids.

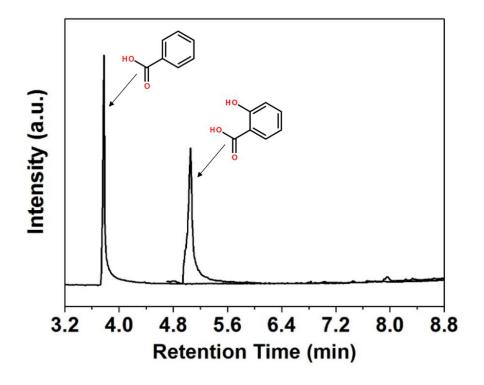


Figure S2. GC-MS chromatogram of the BA/PMS/Co²⁺ reaction sample.

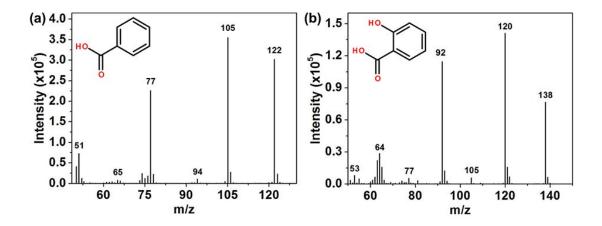


Figure S3. GC-MS spectra of BA (a) and SA (b).

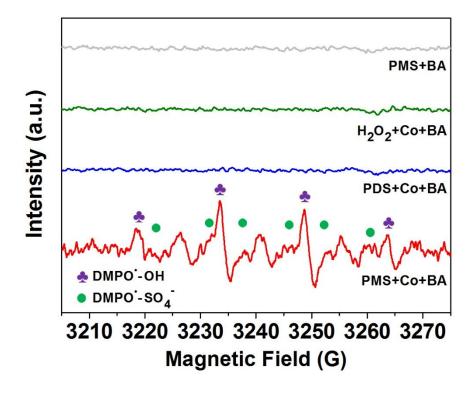


Figure S4. EPR spectra in the activation of PMS under different conditions.

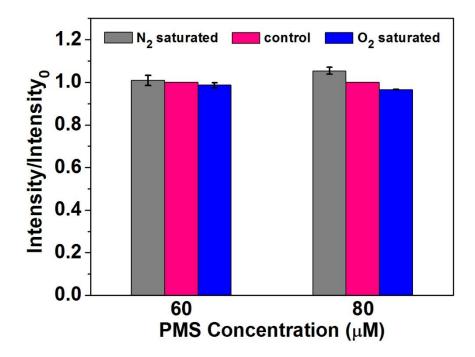


Figure S5. Impact of atmosphere conditions on the fluorescence intensity of the BA/PMS/Co²⁺ system. Reaction conditions: [BA] = 10 mM, $[Co^{2+}] = 50 \mu M$, and solution pH = 6.5.

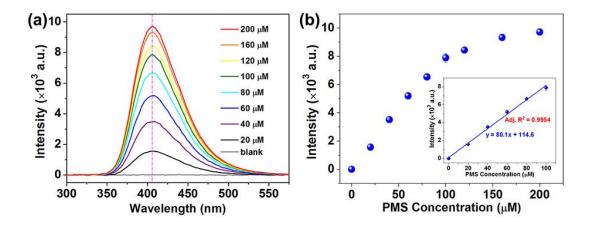


Figure S6. Fluorescence emission spectra at different PMS concentrations (a), relationship between fluorescence intensity and PMS concentration (b) and the corresponding calibration curve (inset in b). Reaction conditions: [BA] = 10 mM, $[Co^{2+}] = 50 \mu M$, and solution pH = 6.5.

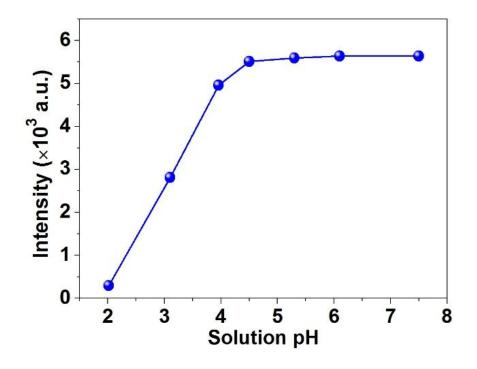


Figure S7. Effect of solution pH on the fluorescence intensity of SA solution.

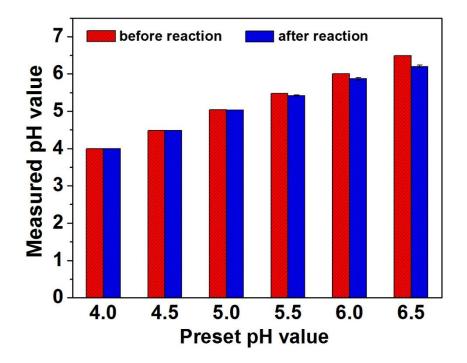


Figure S8. Solution pH changing profiles after 3-min reaction of BA/PMS/Co²⁺ system. Reaction conditions: [PMS] = 80 μ M, [BA] = 10 mM, [Co²⁺] = 50 μ M.

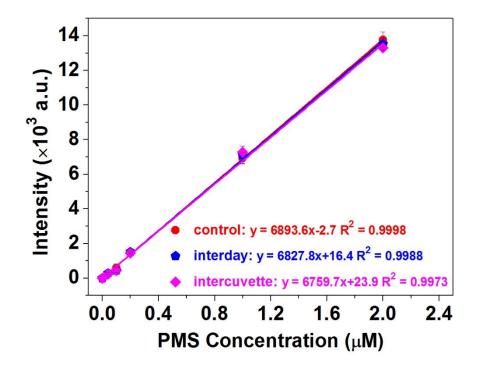


Figure S9. Calibration curves of PMS obtained on different dates and with different cuvettes. Reaction conditions: [BA] = 20 mM, $[Co^{2+}] = 50 \text{ }\mu\text{M}$ and solution pH = 5.5.

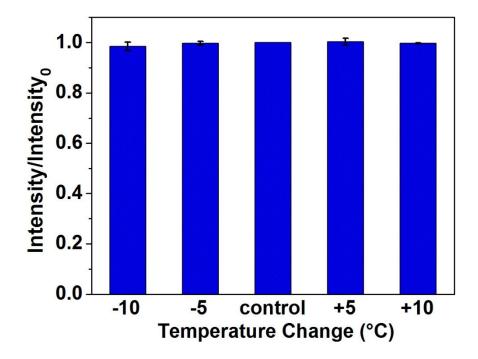


Figure S10. Impact of reaction temperature on PMS determination in BA fluorometry. Reaction conditions: [PMS] = 80 μ M, [BA] = 20 mM, [Co²⁺] = 50 μ M, solution pH = 5.5, and temperature of the control group was 25 °C.

REFERENCES

- Boudeville, P. E. A. Simultaneous determination of hydrogen peroxide, peroxymonosulfuric acid, and peroxydisulfuric acid by thermometric titrimetry. *Anal. Chem.* 1983, 55, 612-615.
- (2) Zhang, T.; Zhu, H. B.; Croué, J. P. Production of sulfate radical from peroxymonosulfate induced by a magnetically separable CuFe₂O₄ spinel in water: Efficiency, stability, and mechanism. *Environ. Sci. Technol.* **2013**, *47*, 2784-2791.
- (3) Zinchuk, V. K.; Stadnichuk, E. N. Chemiluminescence Determination of Monopersulfuric Acid. J. Anal. Chem+. 2001, 56, 918-919.
- (4) Wacławek, S.; Grübel, K.; Černík, M. Simple spectrophotometric determination of monopersulfate. *Spectrochim. Acta A* 2015, *149*, 928-933.
- (5) Gokulakrishnan, S.; Mohammed, A.; Prakash, H. Determination of persulphates using N,N-diethyl-p-phenylenediamine as colorimetric reagent: Oxidative coloration and degradation of the reagent without bactericidal effect in water. *Chem. Eng. J.* 2016, 286, 223-231.
- (6) Zou, J.; Ma, J.; Zhang, X.; Xie, P. Rapid spectrophotometric determination of peroxymonosulfate in water with cobalt-mediated oxidation decolorization of methyl orange. *Chem. Eng. J.* 2014, 253, 34-39.
- (7) Zhang, J. Q.; Ma, J.; Zou, J.; Chi, H. Z.; Song, Y. Spectrophotometric determination of peroxymonosulfate anions via oxidative decolorization of dyes induced by cobalt. *Anal. Methods-UK* 2016, *8*, 973-978.