Electronic Supplementle Material (ESM)

A high selective fluorescent probe for BO_3^- based on acetate derivatives of coumarin in aqueous solution and thimerosal

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Figure S1: The selectivity of probe for H_2O_2

Figure S2: Theoretical calculation

Figure S3: Detect perborate of thimerosal by employing the interfering agents

Figure S1: The selectivity of probe for H_2O_2

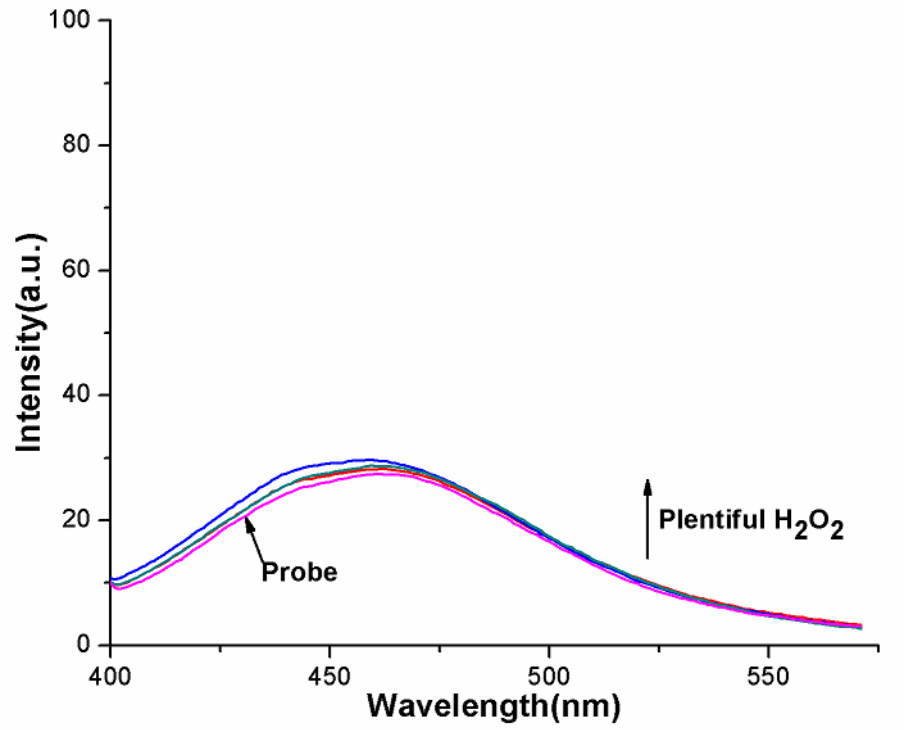

Fig S1. Fluorescence spectral changes of probe (10 μM) in acetate buffered solution (10 mM, pH 5.0) (λ_{ex} = 365 nm, λ_{em} = 452 nm, slit: 5 nm/5 nm) upon addition of plentiful H_2O_2.

Figure S2: Theoretical calculation

In order to further study the optical properties of probe and perborate-induced complex, theoretical predictions based on DFT and the time-dependent DFT (TDDFT) were explored at the B3LYP/6-311++G (d, p) level. As shown in Table S1, the TDDFT calculation confirmed the allowed $S_0 \rightarrow S_1$ electronic transitions with oscillator strength f = 0.1465 and 0.3040 respectively for the **AC** and perborate-induced complex. The calculated excitation wavelengths of AC and perborate-induced complex are 318 and 299 nm respectively which is much closed to the experimentally observation (311 and 280nm). Both the excited states of the two complexes are originated from HOMO→LUMO. On the basis of the frontier molecular orbital (Fig S1), the intramolecular charge transfer (ICT) takes place in AC, while it disappears in perborate-induced complex due to the larger conjugated system. It is well known that the fluorogenic process can be mediated by the ICT mechanism. [S1-S3] Therefore, the ICT process takes place in AC resulting in weaker fluorescence emissions. Compared with AC, such an ICT process is significantly prohibited for the complete conjugated system in perborate-induced complex, and therefore a stronger fluorescence was observed experimentally.

Table S1. Calculated TDDFT excitation properties.

Complex	State	λ_{max} (nm)	f	Dominant excitations
CH_3COO	$S_0 \rightarrow S_1$	318	0.1465	H→L (65.4%)
OH	$S_0 \rightarrow S_1$	299	0.3040	H→L (67.4%)

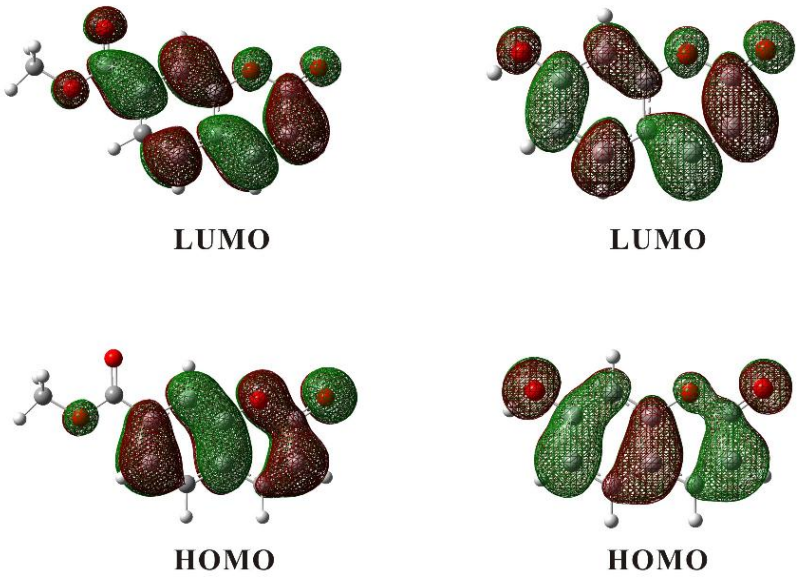

Fig S2a. Calculated HOMO and LUMO of **AC** (left column) and perborate-induced complex (right column).

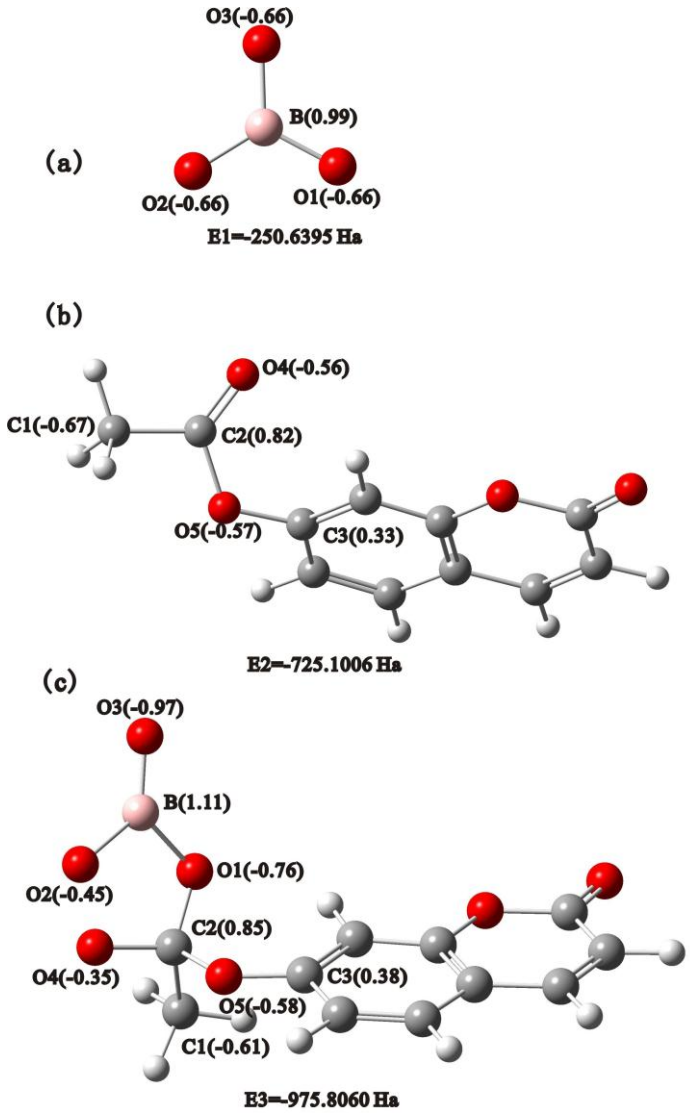

Fig S2b. The optimized structures, natural bond orbital (NBO) charges (in |e|) and single point energy (E, in Ha) of (a) perborate, (b) AC and (c) complex formation between perborate and AC.

S1 H. S. Jung, K. C. Ko, G. H. Kim, A. R.Lee, Y. C. Na, C. Kang, J. Y. Lee, J. S. Kim, *Org. Lett.*, 2011, **13**, 1498-1501.

S2 Q. Li, M. Peng, H. Li, C. Zhong, L. Zhang, X. Cheng, X. Peng, Q. Wang, J. Qin, Z. Li, *Org. Lett.*, 2012, **14**, 2094-2097.

S3 L. Deng, W.Wu, H. Guo, J. Zhao, S. Ji, X. Zhang, X.Yuan, C. Zhang, J. Org. Chem., 2011, **76**, 9294-9304.

Figure S3: Detect perborate of thimerosal by employing the interfering agents.

In the acetate buffered solution (10 mM, pH 5.0) of 2 mL containing the probe (10 μM) and interfering agents, thimerosal was added with 2 μL. From its corresponding fluorescence intensity and work curve, we can obtain the probable concentration of BO_3^- this thimerosal: 0.146 M. The result showed that the probe can specially detect perborate of thimerosal.

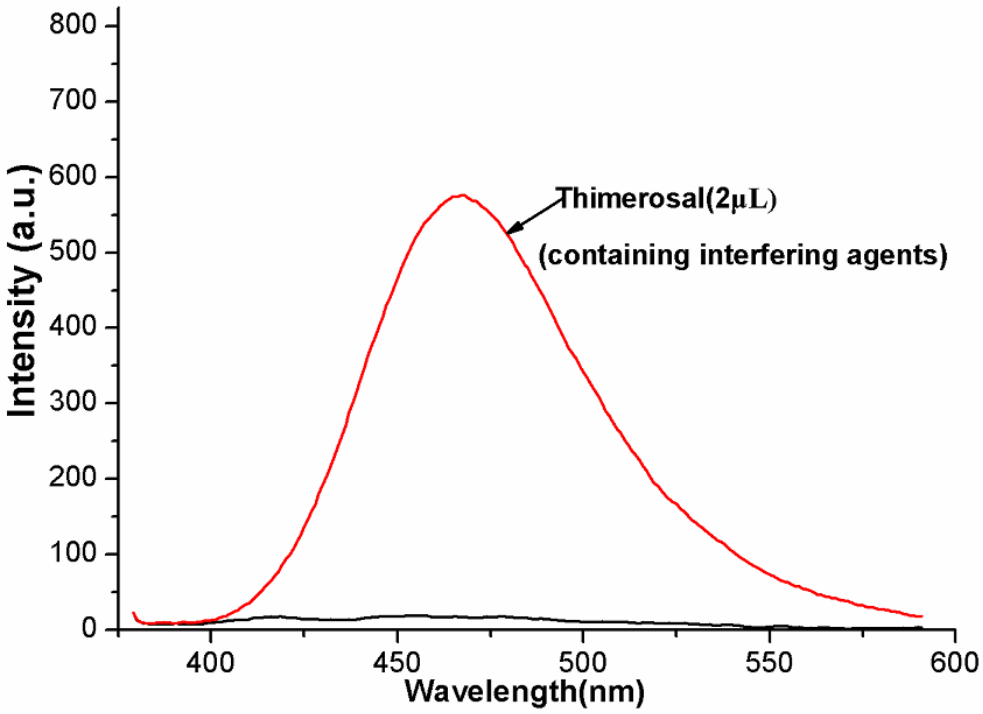

Fig S3. The fluorescence spectral changes determination BO_3^- concentration for thimerosal.