Electronic Supplementary Information

Derivatization-free determination of carbonyl compounds using bifunctional chemiluminescence coreactant thiourea dioxide

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Experimental Section

Chemicals and materials. Luminol was purchased from Ark Pharm. Thiourea dioxide (TD) and diacetyl (DA) were obtained from Aladdin. Benzaldehyde (BZH), sodium pyruvate (PAS), glyoxal (GO), trichloroacetaldehyde hydrate (TCA) and glutaraldehyde (GTA) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). Vanillin (VAN) and 1,3-dihydroxyacetone (DHA) were purchased from Macklin and Accela Chem Bio Co. Ltd. (China), respectively. Formaldehyde (FA) was supplied by Tianjin Dingfu Chemical General Factory (Tianjin, China).
Luminol stock solution (10 mM) was prepared by dissolving 0.0709 g luminol in 0.1 M NaOH. 0.1 M Carbonate buffer solutions (CBS) with different pH values were prepared by Na_2CO_3, $NaHCO_3$, and NaOH. All the chemicals were analytical-reagent grade and were used without further purification. Ultrapure water was used throughout all experiments.

Apparatus. The CL signal was captured by a Biophysics Chemiluminescence (BPCL) ultra-weak luminescence analyzer (the Institute of Biophysics, Chinese Academy of Sciences) in a homemade polymethyl methacrylate CL cell. The cell was put in a

light-tight box of the luminescent analyzer.

Procedure of BZH detection. The procedure for BZH detection was carried out by mixing 100 μL of different concentrations of BZH and 100 μL of 1 mM TD with 700 μL of 0.1 M CBS in the homemade CL cell firstly. After 20 seconds, 100 μL of 10 μM luminol was added rapidly into the above solution and the CL signal was measured immediately. The CL intensities at 80 seconds were used for BZH detection.

Procedure of the detection of other carbonyl compounds. The detection of other carbonyl compounds was carried out by mixing 100 μL of 500 μM different carbonyl compounds and 100 μL of 1 mM TD with 700 μL of 0.1 M CBS in the homemade CL cell firstly. After 20 seconds, 100 μL of 10 μM luminol was added rapidly into the above solution and the CL signal was measured immediately.

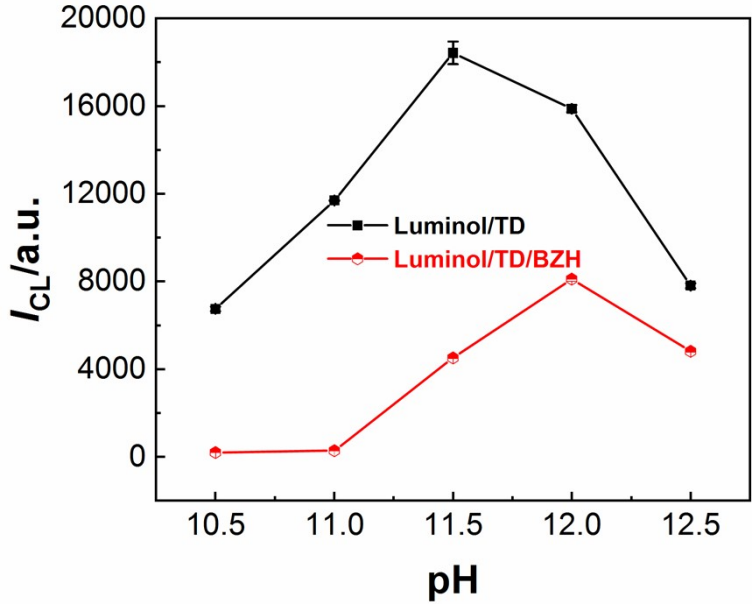

Fig. S1. The effect of pH on the luminol/TD CL and luminol/TD/BZH CL. 1 μM luminol, 1 mM TD, 200 μM BZH; photomultiplier tube voltage: 800 V.

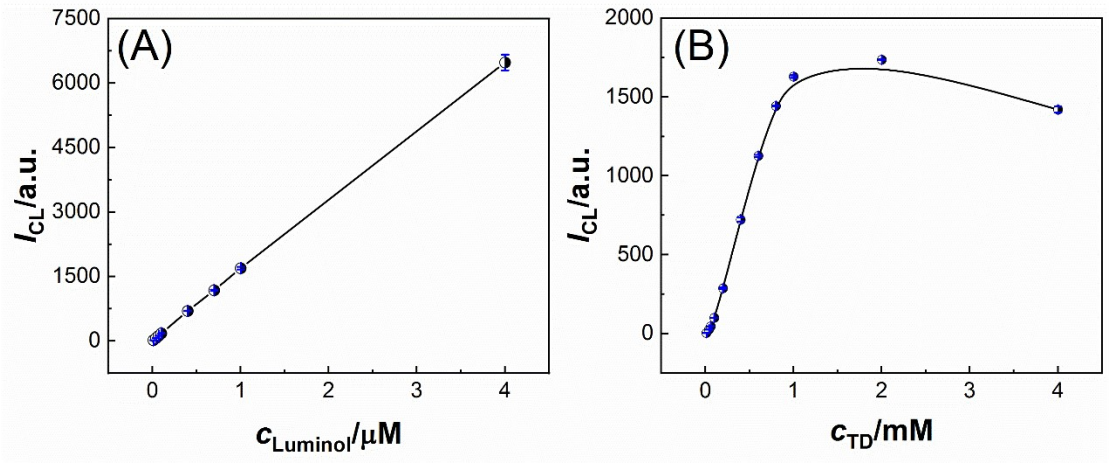

Fig. S2. Interrelation of CL intensity with the concentrations of (A) luminol in the presence of 1 mM TD and (B) TD in the presence of 1 μM luminol; photomultiplier tube voltage: 600 V.

Table S1. Comparison of different analytical methods for BZH detection

Method	Linear range	LOD	Ref
Fluorescence	0.25–5 mM	--	1
Electrochemistry	80–1000 μM	17 μM	2
Fluorescence	0.15–0.9 mM	1.0 μM	3
Fluorescence	0–300 μM	3.43 μM	4
Multi-Responsive Luminescence	50–300 μM	1.1 μM	5
Multi-Responsive Luminescence	50–300 μM	1.3 μM	5
Fluorescence	0.05-05 mM	0.0100 mM	6
Fluorescence	1.0-7.0 mM	0.167 mM	6
Fluorescence	0.5-7.0 mM	0.330 mM	6
Chemiluminescence	3–1000 μM	2.1 μM	This work

LOD: limit of detection.

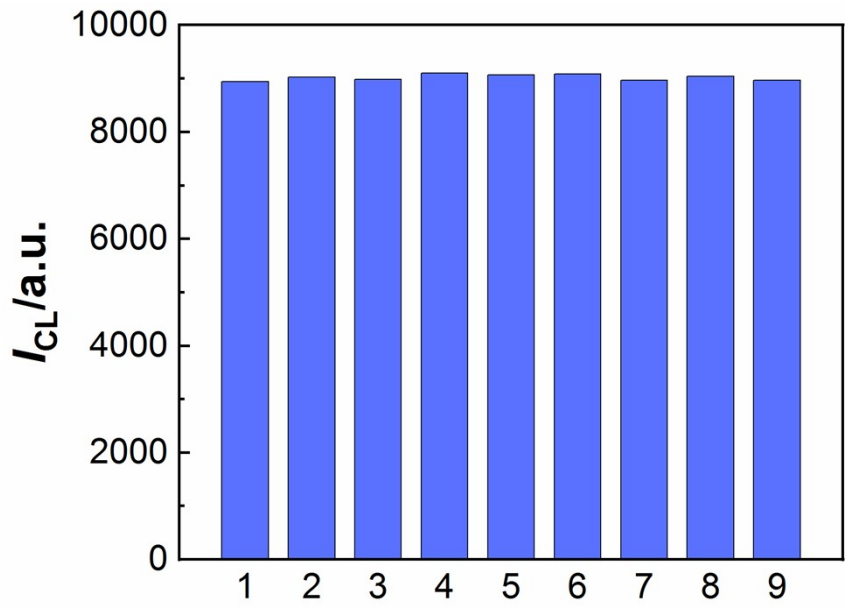

Fig. S3. Reproducibility for the measurement of CL of luminol/TD/BZH system. luminol: 1 μM, TD: 1 mM, BZH: 20 μM; photomultiplier tube voltage: 700 V.

Table S2. Comparison of the quenching effect of different carbonyl compounds on luminol/TD CL

Analyte	I^b	$(I^b/I_0^a)^c$
Blank[a]	10594.33	1.000
Formaldehyde	10482.67	0.9894
Trichloroacetaldehyde	7451.67	0.7029
Diacetyl	5309.33	0.5010
1,3–dihydroxyacetone	3844.33	0.3628
Sodium Pyruvate	1343.33	0.1268
Vanillin	652.33	0.0615
Glutaraldehyde	566.33	0.0534
Benzaldehyde	60.67	0.0057

[a] I_0 (Blank) represents the CL intensity of the control sample.

[b] I represents the CL intensity of the system after adding different carbonyl compounds.

[c] I/I_0 is the CL quenching efficiency after the addition of the analytes.

References

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