Supplementary Material (ESI) for Chemical Communications

Persistent generation of hydroxyl radicals in Tris-Co(II)complex-H_2O_2 system for long-lasting multicolor chemical lights

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Experimental section

Chemicals and materials. 10 mM luminol stock solution was prepared by dissolving luminol (J&K Scientific Ltd., China) into the 0.1 M NaOH solution. 10 mM $Co(NO_3)_2$ stock solution and 100 mM Tris stock solution were prepared by dissolving $Co(NO_3)_2$•$6H_2O$ (Beijing chemical reagent company, China) and Tris (Solarbio Science & Technology Co., Ltd., China) into ultrapure water (18.2 MU cm, Milli Q, Millipore, Barnstead, CA, USA), respectively. 5% $Ti(SO_4)_2$ solution was prepared by dissolving $Ti(SO_4)_2$ into the 3 M H_2SO_4 solution. 30% (v/v) H_2O_2 was obtained from Beijing chemical reagent company and the working solution was prepared fresh daily before the experiment. Acetone solution was precooled at 4 °C. Superoxide Dismutase (SOD) was obtained from Solarbio Science & Technology Co., Ltd. t-BuOH was purchased from Beijing chemical reagent company. Methocel K4M and Methocel K15M (HPMC) were purchased from Dow chemical and stored in a desiccator. All the chemicals in the experiment were ensured to be analytical grade. The solution of Tris-Co(II) complexes was prepared by mixing $Co(NO_3)_2$ solution with Tris solution in different ratios at room temperature.

Optimization of the chemical light system. Tris-Co(II) complex solution was prepared by mixing cobalt nitrate solution with Tris solution. After mixing Tris-Co(II) complex solution with luminol solution and H_2O_2, an intensive and long-persistent light emission appeared, which

could be observed by naked eye in dark environment (Fig. S1). The CL kinetic behaviour of the proposed system was then investigated by a static injection method in a BPCL luminescence analyzer.[1] The optimal concentration of each component was priority considered. As shown in Fig. S2, the CL intensity and the duration time of the proposed system showed an increase with increasing the concentration of Co(II) from 0.1 mM to 0.25 mM. However, the higher concentrations of Co(II) did not favour the longer CL emission and shorten the duration time of the proposed system. In addition, the CL emission of the proposed system was also depending on the concentration of H_2O_2 (Fig. S3). The duration time of proposed system showed an increase with the increase of H_2O_2 concentration from 2.5 mM to 5.0 mM. When the concentration of H_2O_2 was higher than 5.0 mM, the CL emission of proposed system became unstable. Moreover, the duration time of CL signals in the luminol-Tris-Co(II) complex-H_2O_2 system was gradually increased in the presence of 10 mM to 30 mM Tris, but the CL inhibition was observed when the concentrations of Tris were above 30 mM (Fig. S4). This phenomenon might be ascribed to the fact that the reactive sites of Co(II) could almost be occupied in the presence of excessive chelating agents, leading to an inhibition of ·OH generation.[2] Moreover, the pH value of luminol-Tris-Co(II) complex-H_2O_2 system was also considered (Fig. S5). According to the result, the proposed system showed the longer CL duration time with an increased pH. Since an exorbitant pH (>12.5) could cause the hydrolysis of Co(II) in aqueous solution, we chose the pH=12 system as the optimal pH for further investigation.

Properties of the chemical light system. A 100 μL, 20 mM H_2O_2 solution was injected into a mix solution containing 100 μL luminol (10 mM), 200 μL Tris-Co(II) solution for the long-persistent CL. Moreover, 100μL, 20 mM H_2O_2 solution was injected into a mix solution

containing 100 μL luminol (10 mM), 100 μL $Co(NO_3)_2$ (1 mM) and 100 μL H_2O for the comparison. The concentration dependence of each monomer were also investigated to achieve longer and more stable CL. In addition, in the CPPO-BPEA luminescence system, 10 mM CPPO and 0.2 mg/mL BPEA were prepared by diluted each monomer into the ethyl acetate solution, respectively. As a sensitizer, sodium salicylate was dissolved in deionized water to gain a 1.0 M solution. 100 μL, 0.2 M H_2O_2 solution was injected into the two-layer system containing 100 μL CPPO (10 mM), 100 μL BPEA (0.2 mg/mL) and 100 μL sodium salicylate (1.0 M). The stability of CL in luminol tablet-Tris-Co(II)-PVP-H_2O_2 system was also conducted by periodically taking 500 μL of the reaction liquid into the CL quartz vial and monitored. All the CL signals were monitored by a BPCL luminescence analyzer. The photomultiplier tube (PMT) set a working voltage of -720 V for the CL detection and the integration time of the BPCL analyzer was set at 0.1 s per spectrum. Digital images were shoot by iPhone 8 and the photos were taken with an exposure time of 1/6 s. The luminescence spectra of luminol–Tris-Co(II) complex–H_2O_2 system and the CRET spectra were obtained by the F-7000 fluorescence spectrophotometer with its light source off. The measurements for the luminance of CPPO–BPEA–sodium salicylate–H_2O_2 system and our proposed chemical light systems were measured by Konica Minolta CS-2000 spectroradiometer.

ESR measurements. ESR signals of ·OH were measured on an ESR spectrometer (JEOL, JES-FA 200 spectrometer, Tokyo) at 22 °C. DMPO was used as a spin-trap agent, and 10 μL DMPO (~8.97 M) was added into 990 μL solution containing Tris-Co(II)-H_2O_2 system or Co(II)-H_2O_2 system at different concentrations. The reaction media was periodic collected by capillary tube and detected by ESR spectrometer.

Luminol tablets and the release efficiency. The luminol tablets were prepared by direct compression process. HPMC (containing Methocel K4M and Methocel K15M in different mass ratio), Mgst and luminol were mixed with a mass ratio of. 200: 2: 5. The mixed powder was fully grinded and tableted by the punching machine. The net weight for each tablet was controlled to 0.5 g. For the release efficiency test, the prepared tablets were placed into a 20 mL solution containing 0.025 M NaOH, respectively. 10 μL solution was periodic collected and diluted to 1000 μL for the fluorescence measurements. Fluorescence of luminol solutions were measured by an F-7000 fluorescence spectrophotometer by setting 375 nm as the excitation wavelength. The slit width of the excitation and the emission were set at 5.0 nm and the scanning rate was 1200 nm/min. The calculation of luminol concentration was based on the standard curve (Fig. S15).

GC-MS analysis

GC-MS analysis were performed on a system consisting of the Thermo ISO single quadruple MS and the Thermo TRACE 1300 Gas chromatograph to determine the existence of formaldehyde in Tris-Co(II) complex-H_2O_2 system. TG-WAXMS column and EI source was used for GC-MS analysis. Initially，20 mL reaction media containing 30 mM Tris, 0.25 mM Co(II) and 5 mM H_2O_2 was placed in a head space bottle. After 40 min reaction, 0.2 μL sample from the reaction media was injected into the gas chromatograph.

H_2O_2 encapsulation and the release of H_2O_2. PVP-H_2O_2 complex solution were prepared through the method which was previous reported. PVP (2.22 g) with different MW were dispersed into a 5 M H_2O_2 solution and stirred for 6 h at 4 °C. The colorless solution was transformed to a slightly transparent yellowish solution after the stirring process was finished. The as-prepared PVP-H_2O_2 solutions were then encapsulated in to a tube by using

semipermeable membrane as the parafilm and stored at 4 °C. In order to prove the sustained-release of H_2O_2 in the proposed tube, a traditional titanium sulfate method was carried out to quantify the H_2O_2 in the encapsulated PVP-H_2O_2- H_2O system.[3] After the encapsulated PVP-H_2O_2 tube was placed into 20 mL H_2O solution, 10 μL solutions was periodic collected from the reaction media and diluted into a solution containing 990 μL acetone, 0.1 mL 5 % Ti $(SO_4)_2$ and 0.2 mL ammonia, respectively. For the accurate measurement of the absorbance at 415 nm, the turbid solutions were further diluted by 3 M H_2SO_4 to achieve a transparent state. After 5 minutes reaction, light yellow solutions were transferred to a quartz cell and measured on a Shimadzu UV−3600 spectrophotometer (Tokyo, Japan), respectively. Finally, the variation of H_2O_2 concentration in the reaction media was calculated based on the standard curve of H_2O_2 (Fig. S16).

Supporting Figures

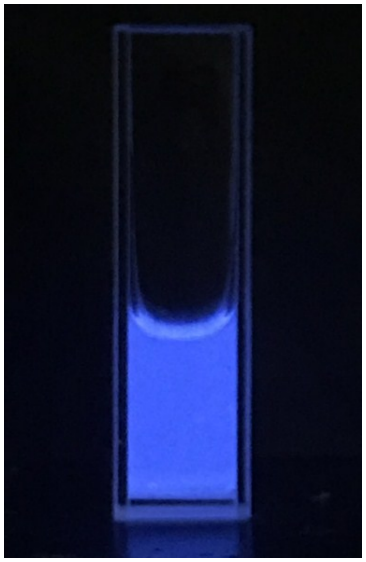

Fig. S1 The CL emission of luminol-Tris-Co(II)-H_2O_2 system.

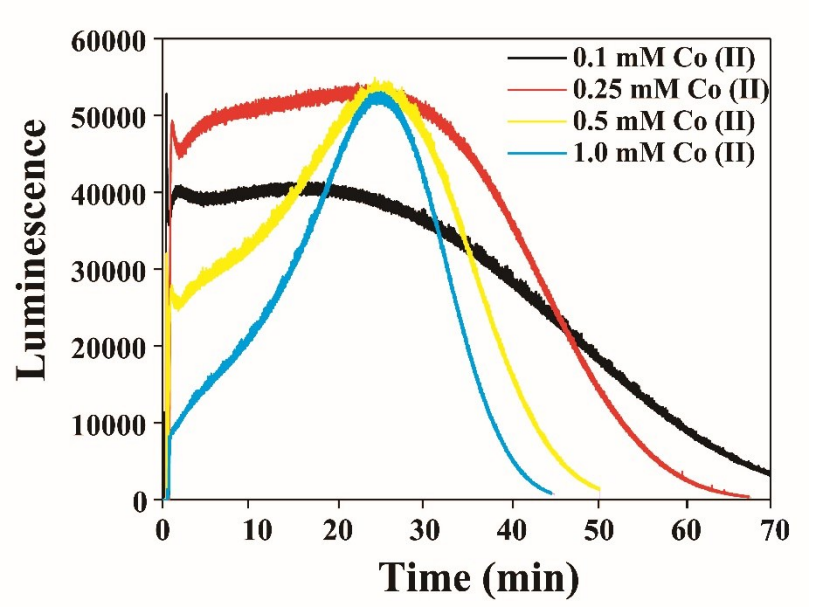

Fig. S2 Influence of Co(II) concentration on the luminol (2.5 mM) CL reactions in the presence of 30 mM Tris and 5.0 mM H_2O_2 under alkaline condition, PMT Voltage = -720 V.

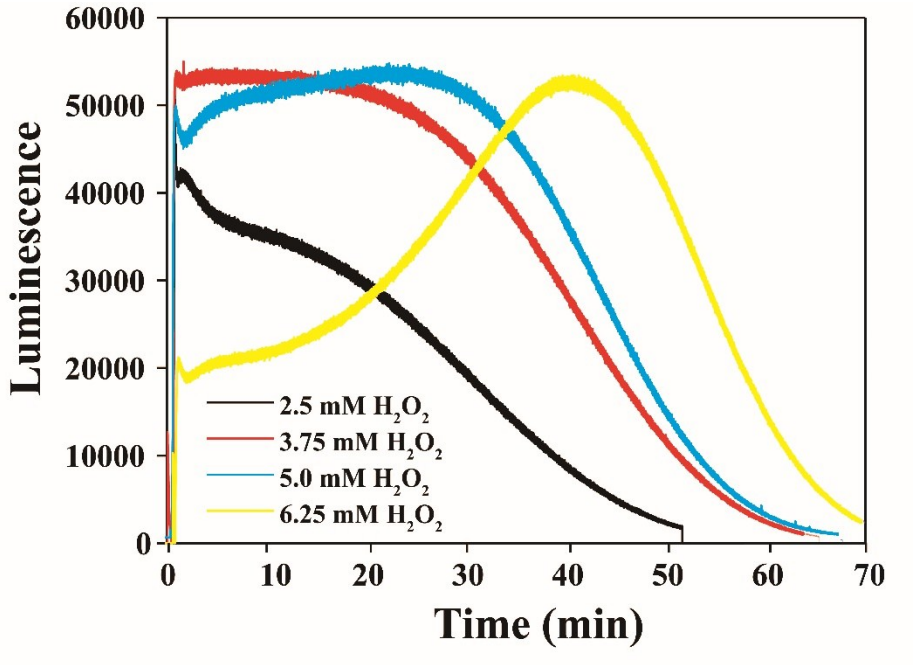

Fig. S3 Influence of H_2O_2 concentration on the luminol (2.5 mM) CL reactions in the presence of Tris (30 mM)-Co(II) (0.25 mM) complexes under alkaline condition, PMT Voltage = -720 V.

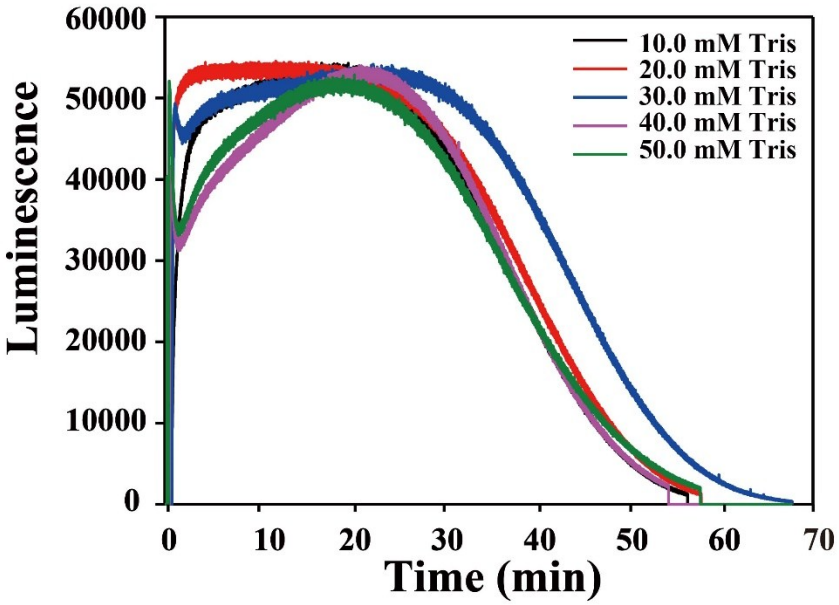

Fig. S4 Influence of Tris concentration on the luminol (2.5 mM) CL reactions in the presence of 5.0 mM H_2O_2 and 0.25 mM Co(II) under alkaline condition, PMT Voltage = -720 V.

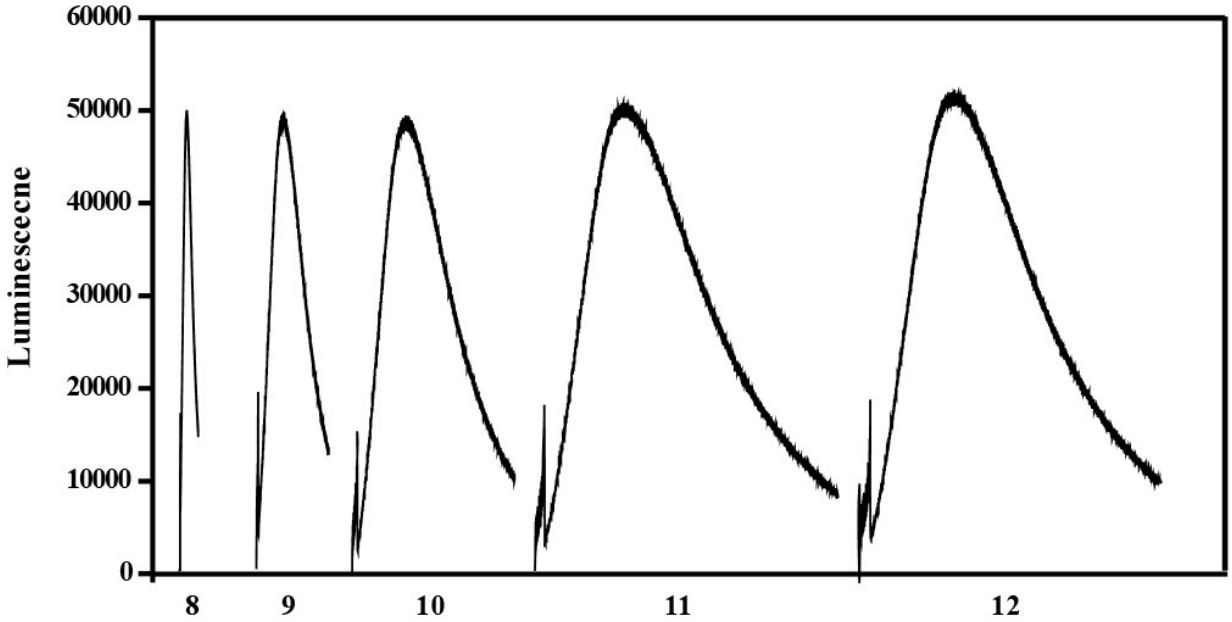

Fig. S5 Influence of pH value in the luminol (2.5 mM)-Tris (30 mM)-Co(II) (0.25 mM)-H_2O_2 (5.0 mM) system, PMT Voltage = -720 V.

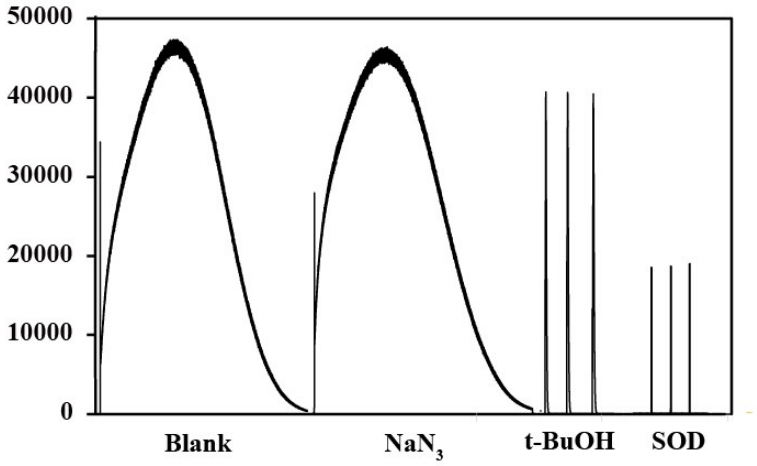

Fig. S6 Effects of NaN_3 (100 mM), *t*-BuOH (50 mM) and SOD (0.5 mM) as radical scavengers on the CL reactions of luminol–Tris-Co(II) complex–H_2O_2 system under alkaline condition, PMT Voltage = -720 V.

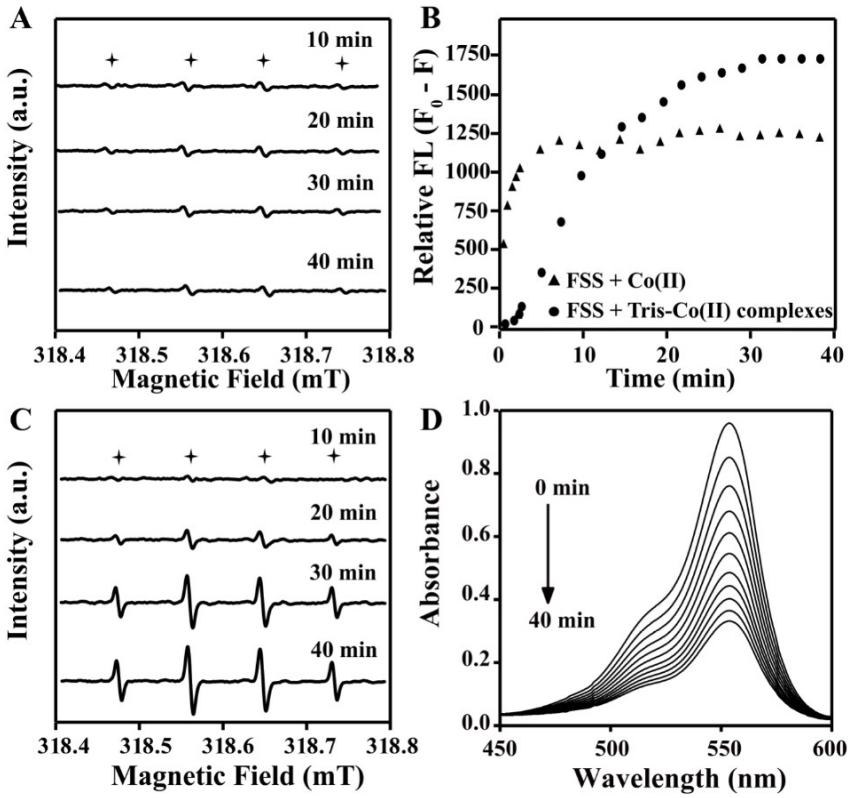

Fig. S7 (A) ESR spectra of DMPO- ·OH adduct in the Co(II) (0.25 mM)-H_2O_2 (5.0 mM) system. DMPO-·OH peaks are depicted by stars. (B) Relative FL kinetic curve of fluorescein sodium salt (10 μM) in the Co(II) (0.25 mM)-H_2O_2 (5.0 mM) or Tris (30 mM)-Co(II) (0.25 mM) complex-H_2O_2 (5.0 mM) system under alkaline condition. F_0 is the initial fluorescence emission of 10 μM FSS solution, F is the fluorescence emission of 10 μM FSS at different time during the reaction process. Ex = 490 nm, PMT Voltage = 700 V. (C) ESR spectra of DMPO-·OH adduct in the Tris (30 mM)-Co(II) (0.25 mM) complex-H_2O_2 (5.0 mM) system under alkaline condition. DMPO-·OH peaks are depicted by stars. (D) UV-vis spectra variation of Rh B (10 μM) in Tris (30 mM)-Co(II) (0.25 mM) complex-H_2O_2 (5.0 mM) system under alkaline condition.

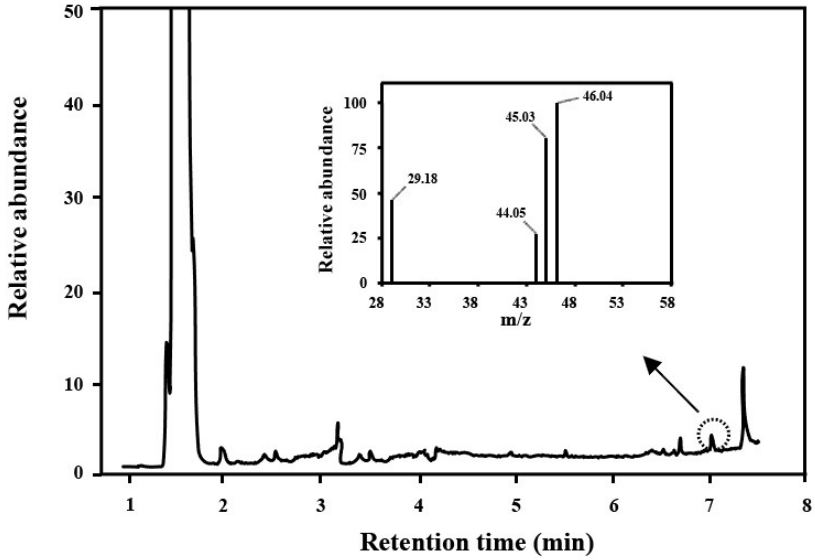

Fig. S8 GC chromatography and the mass spectra (inset) of the media sample in Tris-Co(II)-H_2O_2 system.

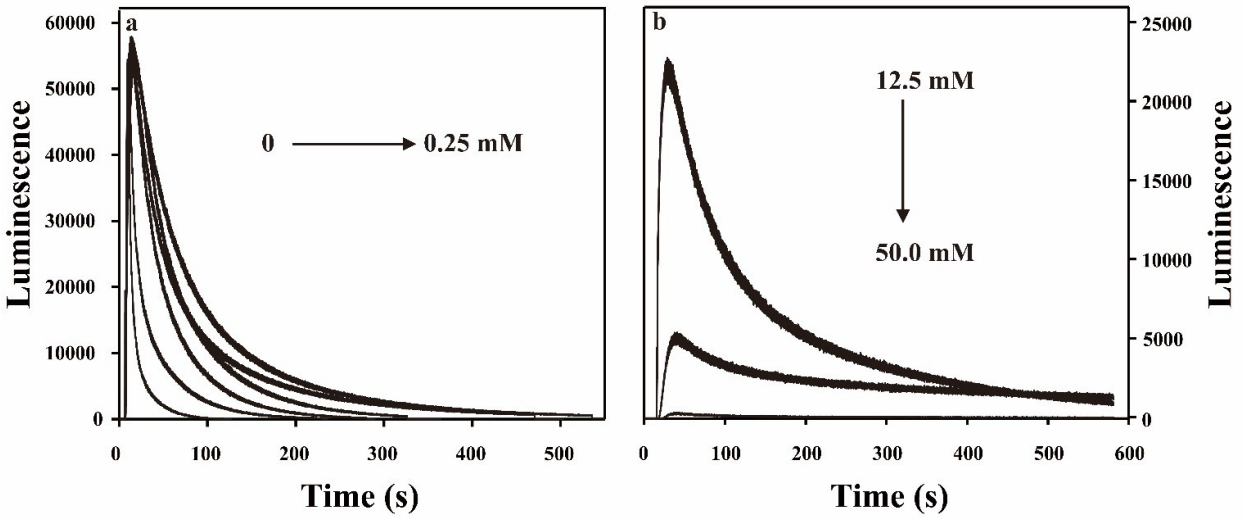

Fig. S9 (a) Influence of 0–0.25 mM ethanolamine on the luminol (2.5 mM) CL reactions in the presence of 5.0 mM H_2O_2 and 0.25 mM Co(II) under alkaline condition. (b) Influence of 12.5–50.0 mM ethanolamine on the luminol (2.5 mM) CL reactions in the presence of 5.0 mM H_2O_2 and 0.25 mM Co(II) under alkaline condition. PMT Voltage = -720 V.

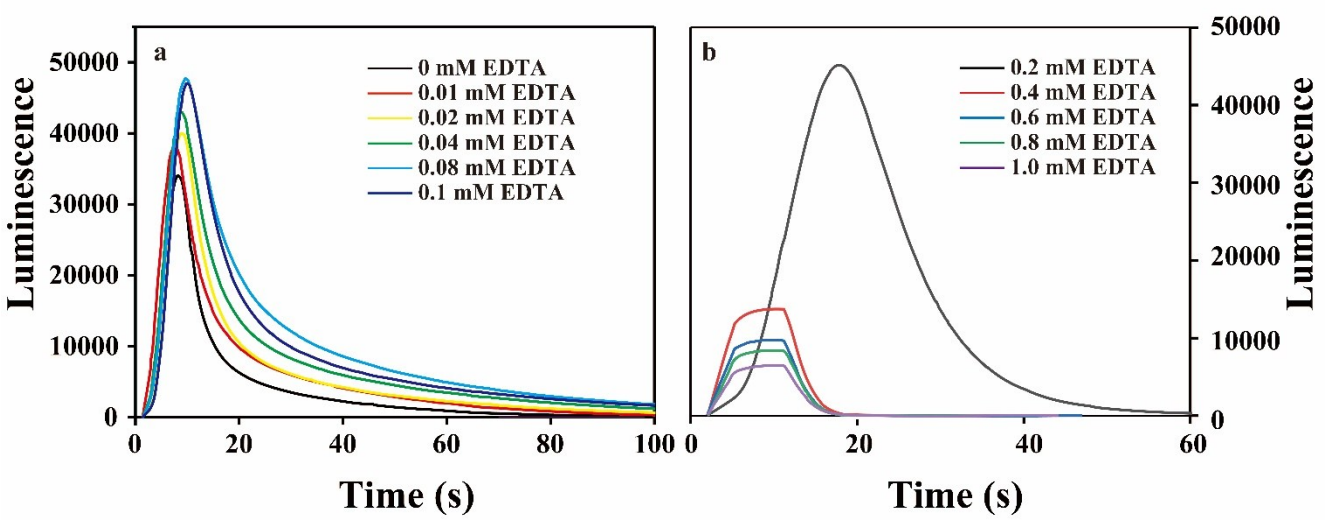

Fig. S10 (a) Influence of 0–0.025 mM EDTA on the luminol (2.5 mM) CL reactions in the presence of 5.0 mM H_2O_2 and 0.25 mM Co(II) under alkaline condition. (b) Influence of 0.05–0.25 mM EDTA on the luminol (2.5 mM) CL reactions in the presence of 5.0 mM H_2O_2 and 0.25 mM Co(II) under alkaline condition. PMT Voltage = -720 V.

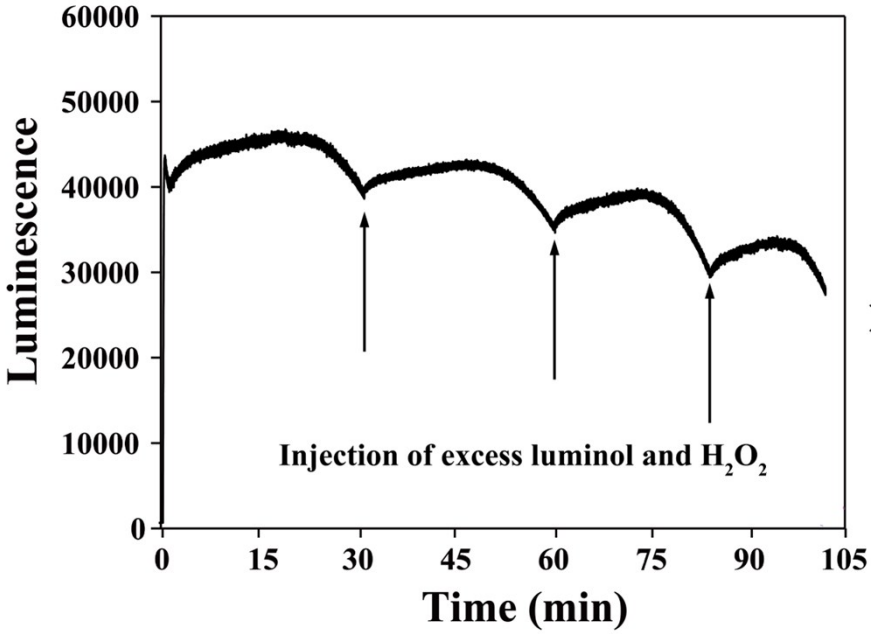

Fig. S11 Influence of excess adding luminol (2.5 mM, final concentration) and H_2O_2 (5 mM, final concentration) on the proposed CL system after the proposed system was reacted for ~30 min.

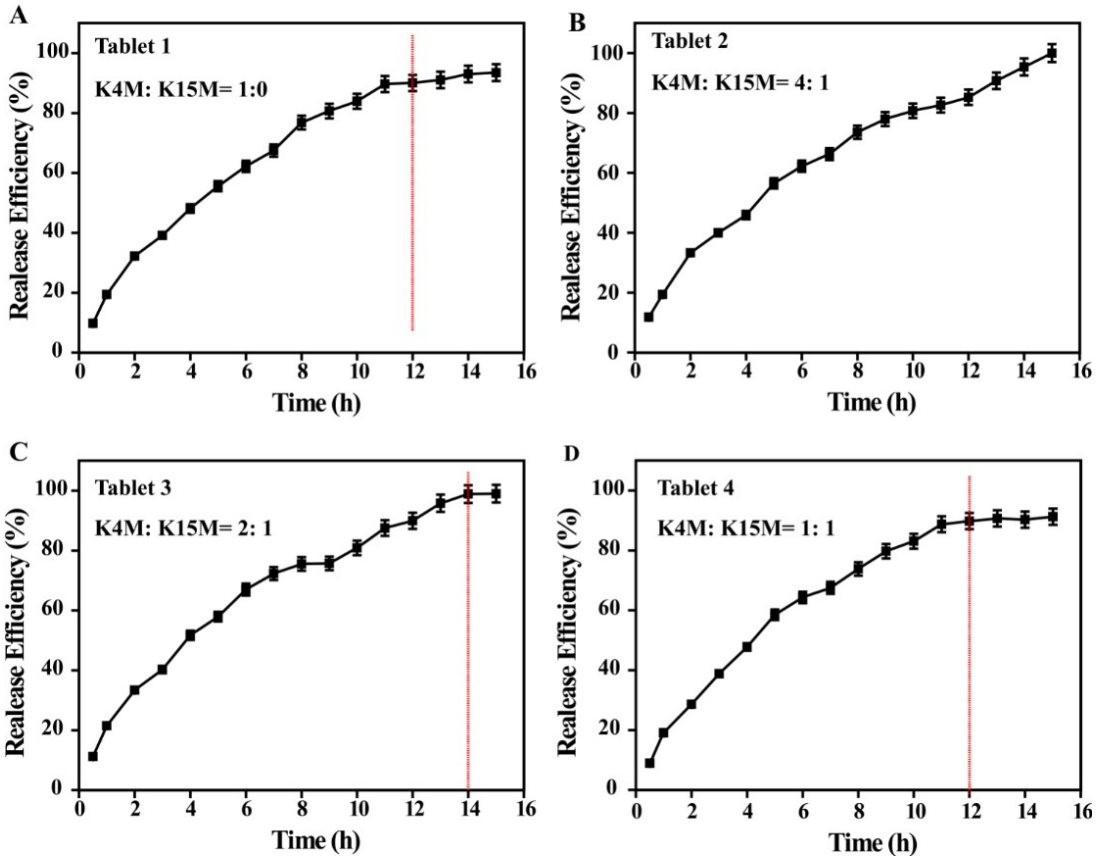

Fig. S12 The release efficiency of the prepared luminol-HPMC-Mgst tablets in 0.025 M NaOH solution.

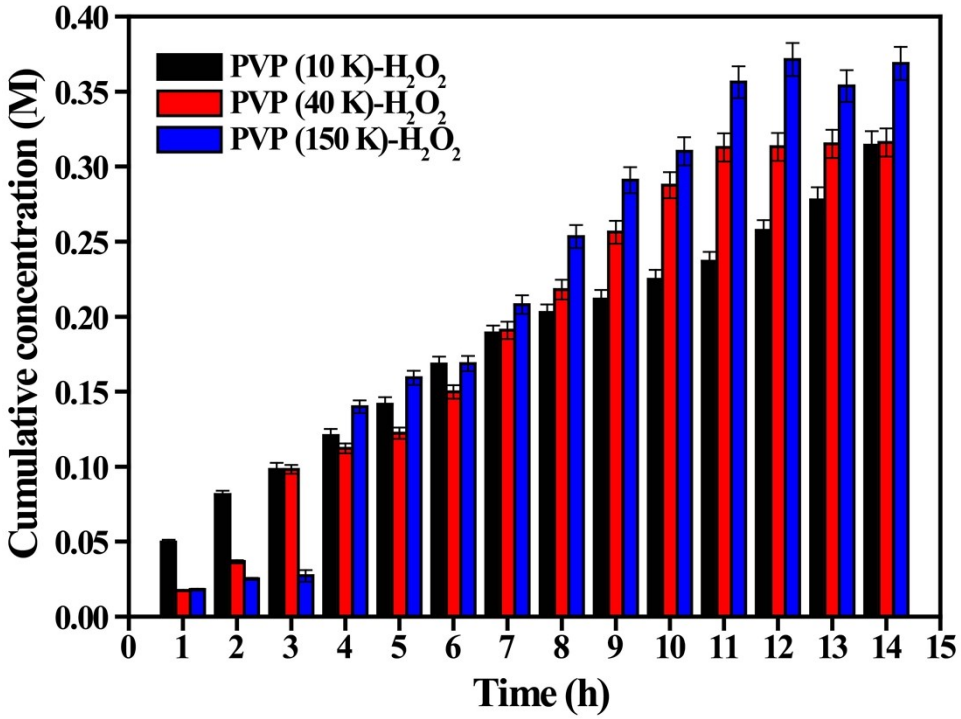

Fig. S13 The cumulative concentration of released H_2O_2 in PVP (10 K)-H_2O_2 system, PVP (40 K)-H_2O_2 system and PVP (150 K)-H_2O_2 system.

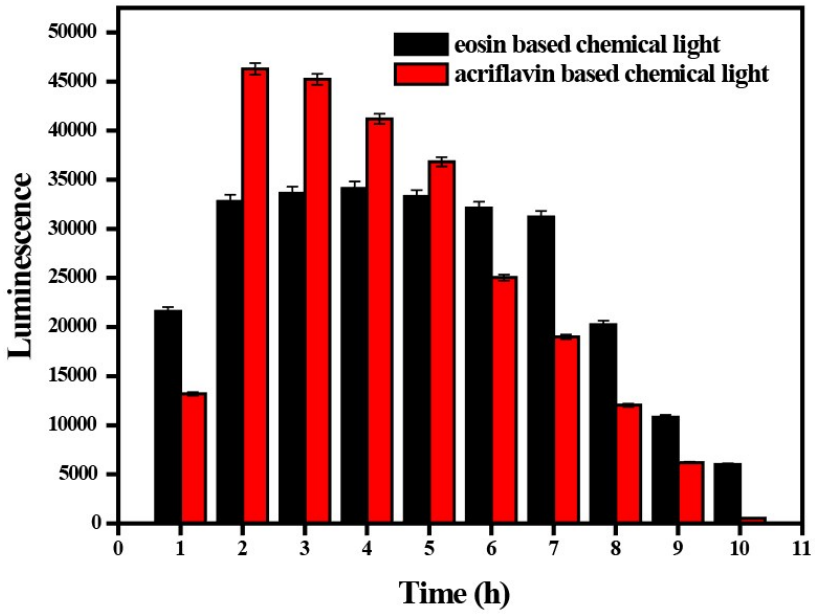

Fig. S14 The stability of CL intensity in eosin (100 μg/mL) based CRET system and acriflavin (25 μg/mL) based CRET system recorded by BPCL luminescence analyzer.

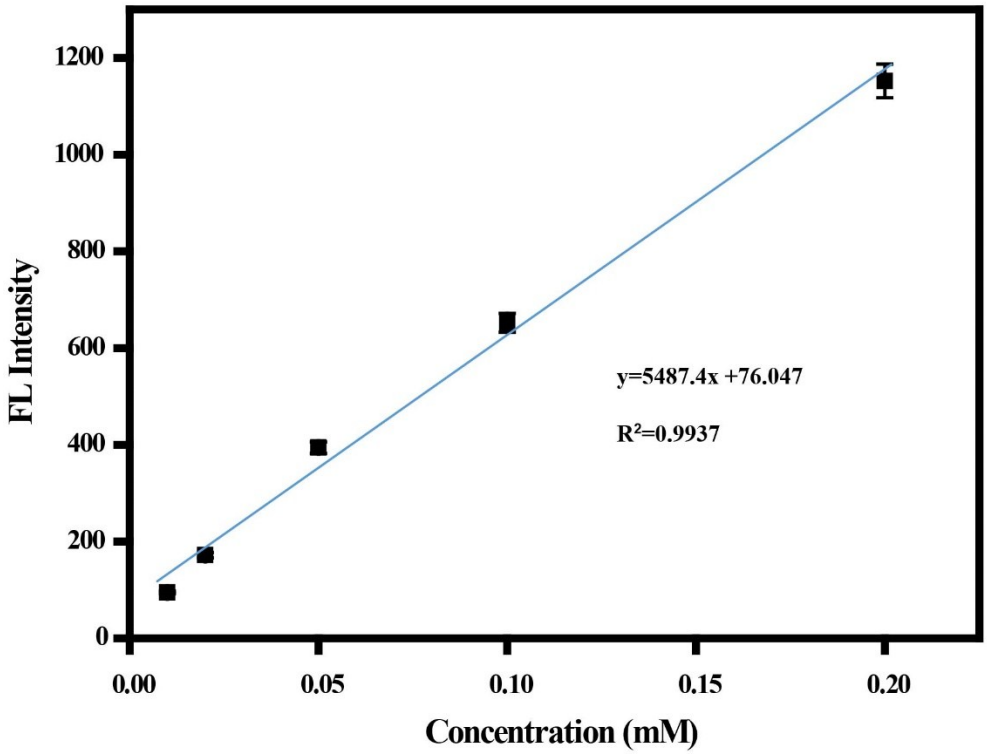

Fig. S15 The standard curve of FL intensity at 415 nm of luminol versus the concentration of luminol

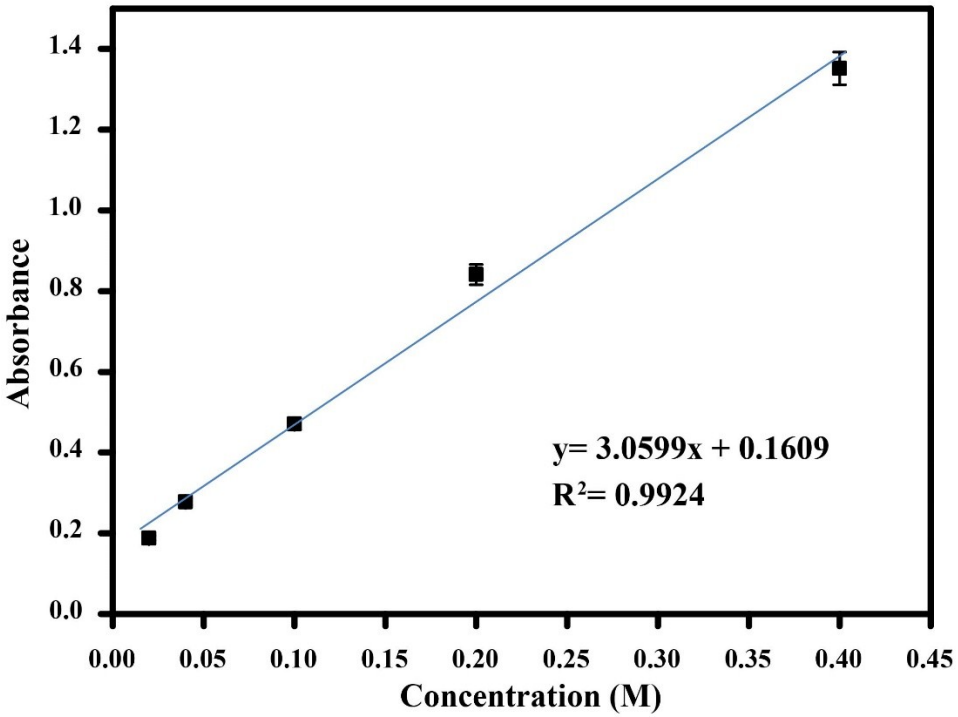

Fig. S16 The standard curve of absorbance at 415 nm of Titanium peroxide versus the concentration of H_2O_2.

Fig. S17 The image of luminol tablet, Tris-Co(II) complexes solution and encapsulated H_2O_2-PVP tube (From left to right).

Table S1 CRET efficiency of luminol-Tris-Co(II)-H_2O_2 system in the presence of different concentrations of eosin and acriflavin.

$C_{acriflavin}$ (μg/ mL)	CRET efficiency (%)	C_{eosin} (μg/ mL)	CRET efficiency (%)
2.5	26.7	2.5	1.2
5.0	26.2	5.0	2.0
10	32.3	10	5.2
15	34.2	25	9.4
20	47.2	50	14.8
25	68.1	100	33.6
30	56.7	250	32.5

Table S2 Luminance characteristics for CPPO–BPEA–sodium salicylate–H_2O_2 system and luminol–Tris-Co(II) complex–H_2O_2 system in the presence of different fluorophores under alkaline condition.

System	Luminance (cd/m^2)
CPPO–BPEA–sodium salicylate–H_2O_2	0.8722
Luminol–Tris-Co(II) complex–H_2O_2	0.6566
Luminol–Tris-Co(II) complex–acriflavin–H_2O_2	0.7416
Luminol–Tris-Co(II) complex–eosin–H_2O_2	0.3287

References

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2. W. Y. Huang, M. Brigante, F. Wu, C. Mousty, K. Hanna and G. Mailhot, *Environ. Sci. Technol.*, 2013, **47**, 1952-1959.

3. C. N. Satterfield and A. N. Bonnell, *Anal. Chem.*, 1955, **7**, 1174-1175.