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ABSTRACT: Forensic luminol chemiluminescence test is one of the most sensitive and popular methods for the determination of latent bloodstains. It mainly uses hydrogen peroxide or sodium perborate as coreactants. The easy decomposition of hydrogen peroxide and sodium perborate in the presence of many ions significantly affects the selectivity. Artemisinin is a natural peroxide that is quite stable in the presence of common ions. In the present study, artemisinin has been exploited for the forensic bloodstain chemiluminescence detection for the first time. Using smart phone as cost-effective portable detector, the visual detection of bloodstains has been achieved with a dilution factor of blood upto 100000. Moreover, this system shows excellent selectivity against many common species. It can well differentiate bloodstains from other stains, such as coffee, brown sugar, and black tea. Both favourable sensitivity and selectivity makes the present method promising in forensic detection.

Blood evidence is one of the most common traces at crime scenes and can provide valuable information in the forensic investigation of violent crimes.[1] It is important to identify any stain that could potentially be blood at a crime scene.[2] The most commonly used method for the visualization of latent bloodstains in criminal investigations uses luminol which could react with the heme groups of blood to produce chemiluminescence (CL).[3] Despite the advantages of high sensitivity and ease of use, the traditional luminol chemiluminescence systems including luminol/H_2O_2/NaOH and luminol/$NaBO_3$/Na_2CO_3 usually suffer from interferences from a variety of common species, such as transition metal ions and metal complexes, which may cause false positives.[4] Thus it is necessary to develop more selective systems for forensic bloodstain determination.

Artemisinin is 2015 Nobel Prize-winning traditional Chinese medicine for the standard treatment of malarial.[5-9] It is a unusual natural peroxide that is quite stable in the presence of common species.[10] Its endoperoxide linkage can be cleaved by hemin to generate reactive oxygen species that can react with luminol to emit light.[11-12]

In this study, artemisinin was used for both the CL detection of hemin and the forensic detection of blood for the first time. Using smart phone as detector, the sensitive visual detection of hemin has been achieved and a good linear relationship of the CL emission intensity with the concentrations of hemin has been obtained. Further, the detection and imaging of blood was investigated. Most importantly, this CL system shows high selectivity against common interferents of traditional luminol CL systems for the forensic detection of bloodstain, meeting the need of forensic bloodstain visualization.

EXPERIMENTAL SECTION

Chemicals and apparatus. Luminol and artemisinin were bought from TCI (Shanghai, China). $CaCl_2$, $CoCl_2$, $MgSO_4$, $AgNO_3$, $Pb(CH_3COO)_2$, $CuSO_4$, $ZnCl_2$, and sodium borate were supplied by Beijing Chemical Reagent Company (Beijing, China). L-Valine (Val), L-proline (Pro), DL-Alanine (Ala), L-Glutamic Acid (Glu), L-Methionine (Met), L-Arginine (Arg), D-Phenylalanine (Phen), D-Aspartic acid (Asp) were bought from Shanghai Yuanju Biotechnology Co. Ltd. (Shanghai, China). Ethylenediaminetetraacetic acid disodium salt (EDTA) was bought from Shanghai Sangon Company (Shanghai, China). Hemin and thiourea were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Superoxide dismutase (SOD) and sodium azide (NaN_3) was purchased from Beijing HWRK Chem. Co. Ltd (China) and Tianjin Fuchen Chemical Reagents Factory (China), respectively. Human whole blood was obtained from local hospital. Luminol and hemin stock solution were prepared by dissolving certain amount of luminol or hemin in 0.1 M NaOH solution. Blood samples were diluted by 0.1 M NaOH solution. Artemisinin was dissolved in ethanol. Carbonate buffer solution with different pH was prepared by sodium bicarbonate, sodium carbonate and sodium hydroxide. All the

other reagents were used as received. Double-distilled water was used throughout all experiments.

CL intensities were captured by a BPCL ultraweak luminescence analyzer supplied by the Institute of Biophysics, Chinese Academic of Sciences. Unless specifically mentioned, the photomultiplier tube (PMT) voltage was kept at 700 V. A homemade CL cell was used in CL intensity detection experiments. Visual detection was operated in a dark box. The images of the CL emission were captured by Nubia Z7 max smart phone. This smart phone has the setting of slow shutter that can capture bright objects against a dark background. And the long exposure time setting options enables the excellent view of the images.

Experimental procedure

Procedures for hemin detection. 5 μL of 10.0 mM luminol and 85 μL of water were pipetted into 400 μL of 0.1 M pH 12.8 carbonate buffer, and then 5 μL of 5.0 mM artemisinin and 5 μL of different concentrations of hemin were added rapidly into the above solution, mixed and used for CL detection immediately. The CL emission spectrum of this system was measured by using various band pass filters at wavelengths of 400 nm, 425 nm, 440 nm, 460 nm, 490 nm, 535 nm, 555 nm, 575 nm and 620 nm.

Visual detection of hemin. 100 μL of different concentration of hemin was dripped onto a small plastic tube. And then, 200 μL of 1.0 mM luminol solution in pH 12.8 carbonate buffer containing 1.0 mM EDTA and 10 μL of 5.0 mM artemisinin solution in ethanol were rapidly dripped onto the hemin samples for CL imaging. Nubia Z7 max smart phone was used to capture the CL images in its automatic mode and the exposure time was set to be 60 seconds. The light spots on the pictures were analyzed by ImageJ software.

Visual detection of blood. 100 μL of diluted human blood sample was dripped onto a small plastic tube, and then 200 μL of 1.0 mM luminol solution in pH 12.8 carbonate buffer containing 1.0 mM EDTA and 10 μL of 5.0 mM artemisinin solution were added to the diluted human blood samples. Finally, visual detection of blood was done with Nubia Z7 max smart phone.

Testing of bloodstains. 10 μL of 100-fold diluted human blood sample was dripped onto filter paper or other substrates. After it is dried, 10 μL of 0.1 M NaOH solution, 10 μL of 1.0 mM luminol solution in pH 12.8 carbonate buffer containing 1.0 mM EDTA and 10 μL of 5.0 mM artemisinin solution were dripped onto the bloodstains for the CL imaging. For comparison, water, coffee, black tea and brown sugar were also used to make stains on filter paper.

RESULTS AND DISCUSSION

The CL of luminol/artemisinin/hemin. Figure 1 shows the CL intensity-time curves of the system containing different contents. The system of artemisinin/hemin has nearly no CL signal. The CL intensities of luminol, luminol/artemisinin and luminol/hemin are very weak. The CL peak intensity of luminol/artemisinin/hemin is about 360 times higher than that of luminol/artemisinin, indicates that hemin can remarkably catalyze the reaction between luminol and artemisinin.[13] The CL emission spectrum of luminol/artemisinin/hemin was shown in Figure S1. The maximum CL emission wavelength is about 470 nm, which is similar to that reported in literatures. To reveal CL mechanism, we have investigated the dependence of CL intensities on the concentrations of SOD, sodium azide and thiourea which are effective radical scavengers of superoxide radical anion ($O_2^{\bullet-}$), singlet oxygen ($^1O_2$), and hydroxyl radical ($HO^{\bullet}$), respectively.[14-16] As shown in Figure S2, NaN_3 and thiourea had little effects on CL intensities even at a high concentration of 1 mM. In contrast, SOD significantly quenches the CL intensity. These results indicated that $O_2^{\bullet-}$ plays key role in the luminol/artemisinin/hemin CL reaction. Therefore, the CL mechanism is proposed as shown in Scheme 1. Hemin catalyzes the decomposition of artemisinin to generate superoxide radicals. Then superoxide radicals react with luminol anion to produce excited 3-aminophthalate, leading to the light emission.[4, 10-11, 17] The CL can keep glowing for several minutes, facilitating the light capture in visual detection. The reaction kinetics is closely related with the cleaving rate of the endoperoxide linkage of artemisinin to generate effective superoxide radicals. Artemisinin is more stable than hydrogen peroxide and the decomposition of artemisinin is relatively slow. As a result, the reaction luminol/artemisinin/hemin is relatively slow, enabling glowing for several minutes.

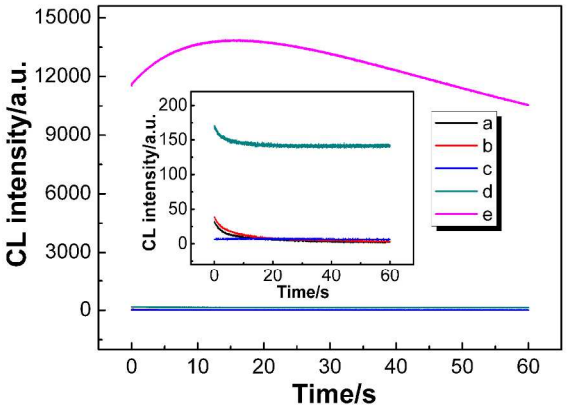
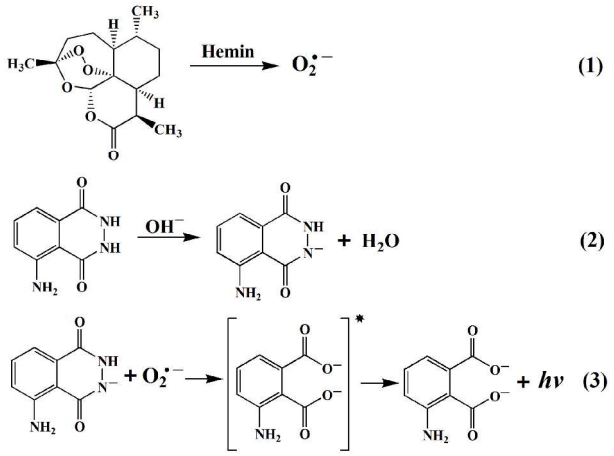


Figure 1. CL intensity-time curves of luminol (a), luminol/artemisinin (b), artemisinin/hemin (c), luminol/hemin (d), luminol/artemisinin/hemin (e). 0.1 M carbonate buffer, pH 12.8; *c*(luminol), 0.1 mM; *c*(hemin), 50.0 nM; *c*(artemisinin), 0.2 mM. Inset is the enlarged curves a, b, c and d.

Scheme 1. The mechanism of luminol/artemisinin/hemin CL system.



Optimization of experimental conditions. To get the best results, the experimental parameters including pH and the concentrations of luminol and artemisinin were optimized. The CL intensity-time curves (Figure S3) show that the CL peak intensities increase as pH increases to 12.8, and the time taken to reach the peak intensity becomes shorter as the pH increase, indicating that the CL reaction becomes faster at higher pH. The increase in peak intensities and reaction rates is attributed to the deprotonation of luminol and the easier decomposition of artemisinin at higher pH. Besides, we tested the CL intensities in different buffer solutions at different pH. Figure S4 shows that the CL intensities are similar at same pH in carbonate buffer solutions, phosphate buffer solutions, and borate buffer solutions, and get the maximum at pH 12.8. It indicates that the composition of buffer has little effect on the detection. The following experiments were carried out in carbonate buffer of pH 12.8 unless otherwise noted.

Moreover, we investigated the influence of concentrations of luminol and artemisinin on CL intensities. As shown in Figure S5, the CL intensities increase as the concentrations of luminol increase to 0.1 mM, and then level off when luminol concentration is higher than 0.1 mM. Thus 0.1 mM of luminol was used in the following experiments. Figure S6 shows the dependence of the CL intensities on artemisinin concentrations. The CL intensity has a good linear relationship with the concentrations of artemisinin, thus this method can be used to detect artemisinin.

Detection of hemin. Under the optimum conditions, the hemin detection based on this new CL system was investigated. Figure 2 shows the dependence of the CL intensities on the concentrations of hemin. The CL intensities increase linearly as the concentrations of hemin increase from 1.0 to 100.0 nM. The linear equation is CL = 7.47 + 18.70*c* (where *c* is the concentration in nM) (R^2 = 0.9956). The limit of detection (LOD) is 0.37 nM at a signal-to-noise ratio of 3. Compared with other reported hemin detection methods,[18-22] as shown in Table 1, this CL method is sensitive and much easier and faster.

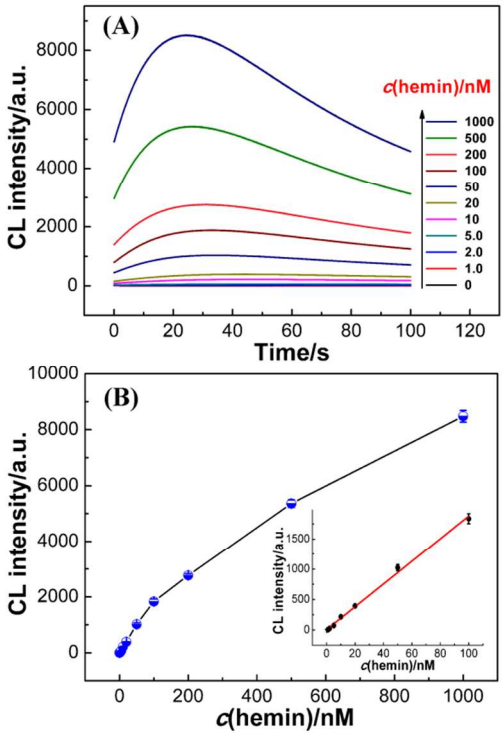


Figure 2. (A) CL intensity-time profiles of different concentrations of hemin. (B) Calibration curve of CL peak intensities versus the concentrations of hemin. Inset is enlarged calibration curve in the range from 1.0 to 100.0 nM. *c*(luminol), 0.1 mM; *c*(artemisinin), 50.0 μM; PMT, 600 V.

The CL signals were detected using a photomultiplier tube (PMT) in the previous sections. However, PMT is somewhat fragile and expensive. For the convenience of bloodstains imaging, it is desirous to develop portable, robust and cost-effective detectors. The visual detection of hemin using mobile phone as detector was thus tested. Figure 3A shows the CL images of hemin from 0.2 to 10.0 μM. The images were analyzed by ImageJ software to quantify the signal over the sample spot area. The obtained numerical value expressed as relative light units (RLU)[23] was used to depict the relationship with the concentrations of hemin. As shown in Figure 3B, a linear calibration curve is obtained from 0.2 to 10.0 μM with a linear equation of CL = 47.79 + 61.44 log (*c*/μM) (R^2 = 0.9918). The detection limit that can be captured is 0.2 μM. Undoubtedly, higher sensitivity can be obtained by extending the exposure time and/or the use of smart phones, cameras or charge-coupled device (CCD) with higher sensitivity.[24]

Table 1. Comparison of different methods for hemin detection.

Methods	probes	Linear range	LOD	Ref.
Electrochemiluminescence	Lucigenin/H_2O_2	0.015 – 15 μM	15 nM	18
Chemiluminescence	Rhodamine B/H_2O_2/NaOH	0.86 – 860 nM	0.086 nM	19
Fluorescence	G-quadruplex structure aptamer/reduced graphene oxide	2.81 – 4.37 μM	50 nM	20
Electrochemistry	Carboxylated graphene/hemin-binding-aptamer functionalized electrode	1– 150 nM	0.64 nM	21
Flame atomic absorption spectroscopy (FAAS)	Task-specific ionic liquid	0.031– 1.23 μM	12 nM	22
Chemiluminescence	Luminol/artemisinin	1–100 nM and 0.2–10.0 μM	0.37 nM	This work

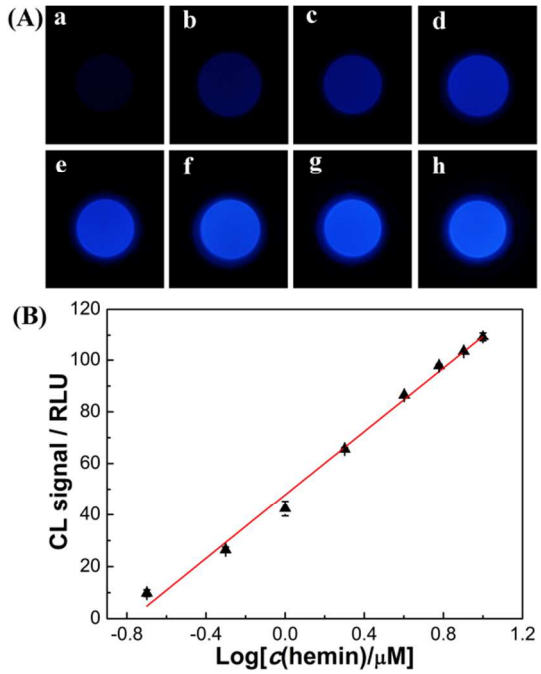


Figure 3. (A) CL images of different concentrations of hemin (μM): a, 0.2; b, 0.5; c, 1.0; d, 2.0; e, 4.0; f, 6.0; g, 8.0; h, 10.0. (B) Calibration curve of CL intensity versus the logarithm of the concentrations of hemin.

Selectivity of the CL method for hemin detection. The selectivity is an important factor to evaluate the performance of one method used in criminal investigation. The traditional CL methods used to test bloodstains are usually interfered by many substances, such as metal ions and some biomolecules.[2, 4, 25-26] Thus in our experiments, the CL intensities of the system in the presence of some metal ions and biomolecules were measured. Since EDTA has little effect on the CL intensity (Figure S7), we added 1.0 mM of EDTA in the detection solution to minimize interferences from metal ions. Figure 4A indicates that common metal ions have little effect on the CL intensities in the presence of EDTA. The biomolecules including amino acids, sugars and urea also have little effect on the CL intensities (Figure 4B). So, this method has good selectivity for hemin detection and is promising for forensic bloodstain testing.

Forensic bloodstain testing. The performance of this approach in bloodstains testing was investigated by capturing the CL images using smart phone. To investigate the detection limit for blood, the blood samples were diluted with 0.1 M NaOH. Dilution factor (DF) was used as the unit to depict the performance of the tests.[3] Figure 5A shows the CL imaging pictures of different dilution factors of blood. As the dilution factor increases, the CL intensity decreases. The CL intensity has a good linear relationship with the logarithm of the dilution factor of blood (Figure 5B). The linear equation is CL = 256.15−51.53 log (DF) (R^2 = 0.9905). The maximum dilution factor of blood detectable by smart phone is 100000. The high detectable dilution factor of blood indicates that this method has good sensitivity and can well satisfy the bloodstains detection in forensic practice.

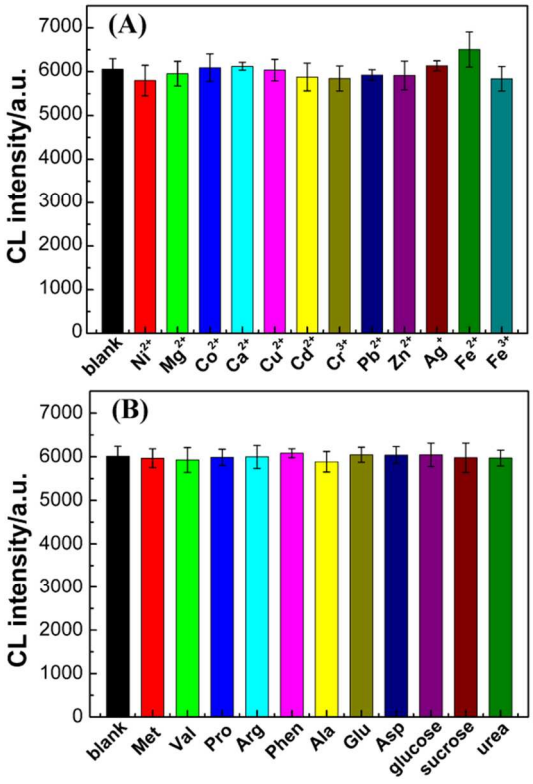


Figure 4. Selectivity of the present method against common metal ions (A) and biomolecules (B). Blank represents the CL system of luminol/artemisinin/hemin. The concentration of all the metal ions is 0.1 mM and the concentration of all the biomolecules is 1.0 mM. *c*(luminol), 0.1 mM; *c*(EDTA), 1.0 mM; *c*(hemin), 50.0 nM; *c*(artemisinin), 0.1 mM.

To better imitate the bloodstains detection in practical applications, we investigated the bloodstains images on different substrates. 100-fold diluted blood samples were deposited on different substrates including plastic (polytetrafluoroethylene), filter paper, cotton, coin and glass. As shown in Figure S8, the upper pictures were blood samples on different substrates taken in daylight before adding luminol and artemisinin solutions, and the lower pictures were taken in a dark box after adding the imaging reagents. The results suggest that substrates have some effect on the visual detection of bloodstains. The different effects may stem from two aspects. On the one hand, the different hydrophobic properties of different materials can greatly affect the diffusion of imaging reagents and thus result in the imaging difference. On the other hand, the color of the substrate can affect the absorption or reflection of the CL emission. Although different substrates have some effects on the bloodstains imaging, the CL emission based on different substrates were all acquired using smart phone. It indicates that this method has nice feasibility and reliability.

To test whether the present method can differentiate bloodstains from other stains, coffee, brown sugar, black tea, water and 100-fold diluted human blood was dripped onto different pieces of 6-mm-diameter filter paper (Figure 6). After it is dried, luminol and artemisinin solutions were dripped onto these samples and used for CL imaging. The corresponding CL images taken in dark box after adding imaging reagents were shown in Figure 6 (a2 to e2). The results suggest that this method can successfully distinguish bloodstain from other stains. It further demonstrates its feasibility in forensic blood-

stain detection. Moreover, we have compared the selectivity of luminol/artemisinin system with luminol/H_2O_2 system using some common metal ions and hypochlorite. Metal ions are widely spread in the environment, such as soils, metal objects, tools and some chemical products.[4, 27-28] Hypochlorite, as the effective component of disinfectants and bleaches,[29-32] is often used in cleaning up murder scenes.[4] Compared with luminol/H_2O_2 system, luminol/artemisinin system has better selectivity toward these metal ions and hypochlorite. As shown in Figure S9, all these species, particularly, cobalt ions and hypochlorite, cause false-positive results using luminol/H_2O_2 system-based detection. Fortunately, luminol/artemisinin CL system can effectively distinguish blood from these species. Thus, the present method shows distinct advantages in selective bloodstain detection over luminol/H_2O_2 system.

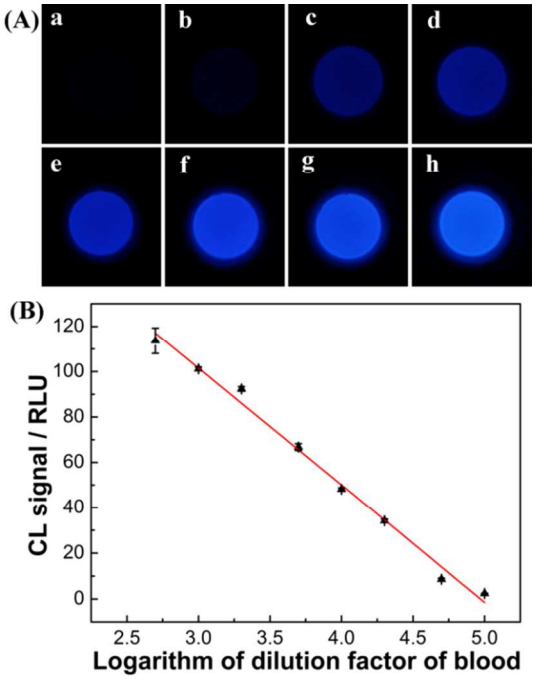


Figure 5. (A) CL images of blood samples of different dilution factors: a, 100000; b, 50000; c, 20000; d, 10000; e, 5000; f, 2000; g, 1000; h, 500. (B) The relationship curve of CL intensities versus the logarithm of the dilution factors of blood.

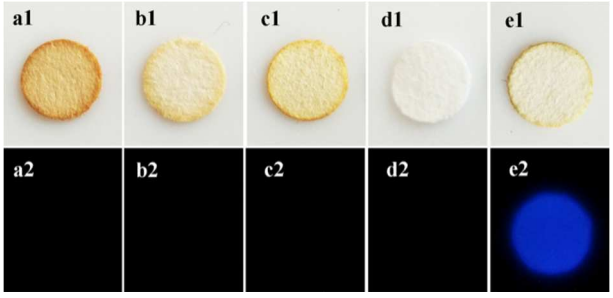


Figure 6. Photos of filter papers with stains of (a1) coffee; (b1) brown sugar, (c1) black tea, (d1) water, and (e1) 100-fold diluted blood, taken in daylight before adding luminol and artemisinin solutions. a2 to e2 are the corresponding CL images taken in a dark box after the addition of the CL imaging reagents.

CONCLUSIONS

Artemisinin has been exploited for the luminol CL detection of both hemin and bloodstain for the first time. The artemisinin-luminol CL method enables the detection of blood with a dilution factor up to 100000 by cost-effective smart phone. Note worthily, it shows excellent selectivity toward common metal ions and biomolecules, and can differentiate bloodstains from other stains, such as coffee, brown sugar, and black tea. Moreover, the sensitivity can be further enhanced by smart phones or cameras using CMOS or CCD with higher sensitivity. In view of both favourable sensitivity and high selectivity, the present method is an appealing alternative for the forensic bloodstain detection.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

The CL spectrum of luminol/artemisinin/hemin system; CL intensity of luminol/artemisinin/hemin in the absence and presence of radical scavengers; the effect of pH, buffer solution, concentrations of luminol and artemisinin, EDTA on CL peak intensity; images of bloodstains on different substrates; comparison between luminol/H_2O_2 and luminol/artemisinin CL system in distinguishing blood from common ions (PDF)

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