

Long-Lasting Chemiluminescence by Aggregation-Induced Emission Surfactant with Ultralow Critical Micelle Concentration

Youkai Yu¹, Zhiqin Yuan¹, and Chao Lu²

¹Beijing University of Chemical Technology

²Affiliation not available

March 8, 2023

Abstract

The development of green and simple chemiluminescence (CL) systems with intensive and long-lasting emission is highly desirable in lighting and extension of their applications. In this study, it is found that the involvement of aggregation-induced emission (AIE) surfactant could greatly enhance the CL of luminol-H₂O₂-Co²⁺ system. The inserted hydrophobic tetraphenylethylene fluorophore in AIE is able to increase the hydrophobicity of alkyl chain and decrease the critical micelle concentration (CMC) of surfactant. The synergistic effect of micelle-improved enrichment and CL resonance energy transfer endows luminol-H₂O₂-Co²⁺ system intensive and long-lasting emission under neutral pH conditions (pH 7.4). The visible emission is still observed even after 60 min. Our study has opened a new avenue for exploring green and simple effective CL systems through AIE surfactant with ultralow CMC toward various applications in lighting, optical sensing, and photocatalysis, etc.

Long-Lasting Chemiluminescence by Aggregation-Induced Emission Surfactant with Ultralow Critical Micelle Concentration

Youkai Yu,¹Zhiqin Yuan*,¹ and Chao Lu*,^{1,2}

¹ Y. Yu, Dr. Z. Yuan and Prof. Dr. C. Lu State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China

E-mail: yuanzq@mail.buct.edu.cn (Z. Yuan), luchao@mail.buct.edu.cn (C. Lu). Phone/Fax: +86 10 64411957.

² Prof. Dr. C. Lu Green Catalysis Center, and College of Chemistry, Zhengzhou University, Zhengzhou 450001, China

Keywords: long-lasting chemiluminescence, fluorescent surfactant, aggregation-induced emission

The development of green and simple chemiluminescence (CL) systems with intensive and long-lasting emission is highly desirable in lighting and extension of their applications. In this study, it is found that the involvement of aggregation-induced emission (AIE) surfactant could greatly enhance the CL of luminol-H₂O₂-Co²⁺ system. The inserted hydrophobic tetraphenylethylene fluorophore in AIE is able to increase the hydrophobicity of alkyl chain and decrease the critical micelle concentration (CMC) of surfactant. The synergistic effect of micelle-improved enrichment and CL resonance energy transfer endows luminol-H₂O₂-Co²⁺ system intensive and long-lasting emission under neutral pH conditions (pH 7.4). The visible emission is still observed even after 60 min. Our study has opened a new avenue for exploring green and simple effective CL systems through AIE surfactant with ultralow CMC toward various applications in lighting, optical sensing, and photocatalysis, etc.

1. Introduction

As a classical cold light, chemiluminescence (CL) has attracted wide research interest in last decades due to its advantages of free light source and low background, which makes CL technique essential in the exploration of lighting systems for various applications, *e.g.*, sensing, bioimaging and rescue operations after disasters.¹⁻⁵ To achieve effective and long-period lighting, a long-lasting emission system is usually required.⁶⁻⁸ However, most existing CL systems show flash-type light emission, which hinders their applications.⁹⁻¹¹ In contrast, CL systems with strong intensity and glow-type emission are more charming to the development of cold light sources. To meet this concern, few CL systems with sustained-release of reactants have been developed *via* introducing hydrogel or tablet.^{12,13} For example, Liu *et al.* reported intensive and long-lasting CL hydrogels by integrating chitosan, *N*-(4-aminobutyl)-*N*-ethylisoluminol and Co^{2+} .¹² With the combination of luminol tablet and PVP- H_2O_2 complex solution, our group constructed a long-lasting (~ 13 h) CL light using Tris- Co^{2+} complex as the catalyst.¹³ Nevertheless, the above fabricated systems were complicated, limiting their wide use. Therefore, it is highly necessary to explore a simple and long-lasting CL system.

It is reported that typical luminol- H_2O_2 - Co^{2+} system possesses relatively slow CL kinetics under neutral pH conditions.¹⁴ Unfortunately, the ultraweak CL intensity of luminol- H_2O_2 - Co^{2+} system at neutral condition hinders its further application. It is generally accepted that the introduction of surfactant could enhance CL intensity of most CL systems.¹⁵⁻¹⁷ For instance, Xie *et al.* found that the CL intensity of peroxyoxalate derivatived- H_2O_2 system can be greatly enhanced upon introducing cetyltrimethylammonium bromide (CTAB, a kind of typical cationic surfactant).¹⁸ However, the previous reports demonstrated that the CL promotion was only implemented with high surfactant concentration, usually above critical micelle concentration (CMC), and CMCs of conventional surfactants are generally in mM level.^{19,20} The requirement of high surfactant concentration is conflicting to the green chemistry and environment friendly. Therefore, the development of surfactant with low CMC is required in order to decrease its usage and side effect to environment.

CL resonance energy transfer (CRET) is usually utilized to further improve CL signals. In this case, additional fluorophores as energy acceptors are required in conventional surfactant-enhanced CL systems. For example, Song *et al.* reported the construction of intensive and long-lasting multicolor CL systems by introducing fluorescein or rhodamine B as the energy acceptor.⁷ Nevertheless, the multicomponent involvement results in system complexity and weak stability. Accordingly, a direct linking of fluorophore into surfactant would make CL system simple. Hence, the introduction of novel surfactant with ultralow CMC and CRET acceptor is appealing for a simple and long-lasting CL system.

Stepanek *et al.* proposed fluorescent block copolymer surfactant by linking *p*-vinyl-9,10-diphenylanthracene (DPA) into polystyrene-*block*-poly(methacrylic acid).²¹ Unfortunately, the aggregation-caused quenching (ACQ) properties of DPA led to weak fluorescence upon forming micelle. The ACQ features of the fabricated fluorescent block copolymer surfactant would restrict its potential applications in CL as the CRET acceptor. In contrast, aggregation-induced emission (AIE) fluorophores show bright emission after aggregates.²²⁻²⁵ It is well-known that Tang's group has explored many AIE fluorophores based on tetraphenylethylene (TPE).²⁶⁻²⁸ By inserting TPE into the backbone of surfactant, our group has reported a few novel fluorescent surfactants with ultralow CMC due to the increased hydrophobicity of alkyl chain ($< 60 \mu\text{M}$).²⁹⁻³³ Herein, we described our attempts to apply the developed AIE surfactants into long-lasting luminol- H_2O_2 - Co^{2+} CL system.³⁴ In a case study, we selected the TPE inserted dodecyltrimethylammonium bromide (4th cationic headgroup, denoted as C_8 -TPE- C_4 TAB) for the CL signal enhancement at pH 7.4. The CL intensity revealed 20-fold increment in the presence of only $80 \mu\text{M}$ C_8 -TPE- C_4 TAB, and glow-type emission appeared. The enhanced CL and long-lasting emission were due to the integration of micelle-mediated reactant enrichment and CRET between luminol and TPE (Figure 1). In other word, the CL reactants were enriched through electrostatic attraction, which subsequently benefits the CL reaction and the CRET process. The long-lasting CL was visible to naked eyes even after 60 min. The proposed fluorescent surfactant-assisted long-lasting emission showed advantages of convenient operation, low surfactant consumption and environment-friendly. The development of simple and green long-lasting CL systems for analytical sensing or lighting is possible by introducing novel fluorescent surfactants with ultralow CMCs.

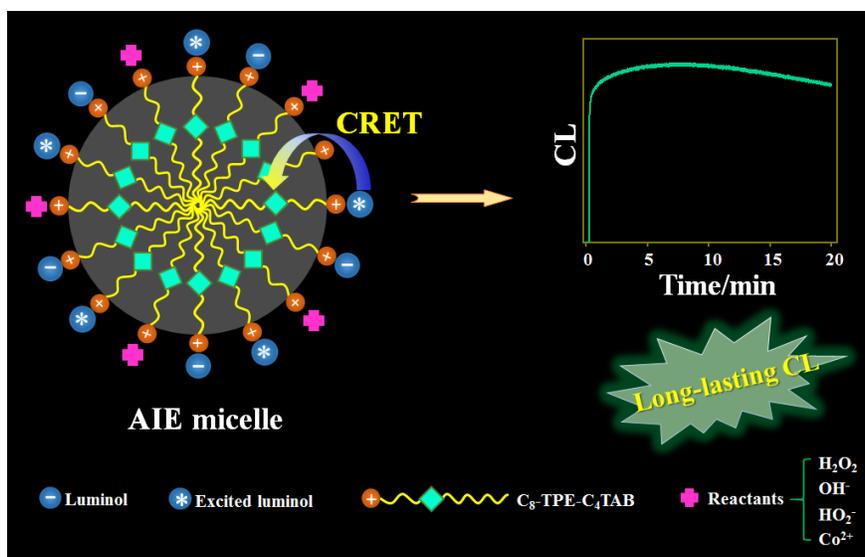


Figure 1. Schematic illustration of C_8 -TPE- C_4 TAB-mediated intensive and long-lasting CL emission of the luminol- Co^{2+} - H_2O_2 system.

2. Results and Discussion

C_8 -TPE- C_4 TAB-enhanced CL of luminol- Co^{2+} - H_2O_2 system. As a starting point for our study, we synthesized fluorescent surfactant C_8 -TPE- C_4 TAB according to our previously reported method and characterized it with 1H NMR, MS, steady-state and time-resolved fluorescence spectrometry.³⁴ All results revealed the successful preparation of C_8 -TPE- C_4 TAB (Figures S1-S3). As is known, surfactants could facilitate the CL reaction and enhance the CL signals.^{35,36} In this study, the CL signals of luminol- Co^{2+} - H_2O_2 in the absence and presence of C_8 -TPE- C_4 TAB were recorded under pH 7.4 conditions. As shown in Figure 2, the CL intensity was dramatically enhanced (~ 20 folds) after the addition of $80 \mu M$ C_8 -TPE- C_4 TAB, indicating the feasibility of C_8 -TPE- C_4 TAB-improved CL intensity of luminol- Co^{2+} - H_2O_2 system. In addition, the reaction kinetics was also dramatically decelerated in the presence of C_8 -TPE- C_4 TAB. The enhanced intensity and extended CL emission kinetics indicated the possibility to construct long-lasting luminol- Co^{2+} - H_2O_2 system with the assistance of C_8 -TPE- C_4 TAB.

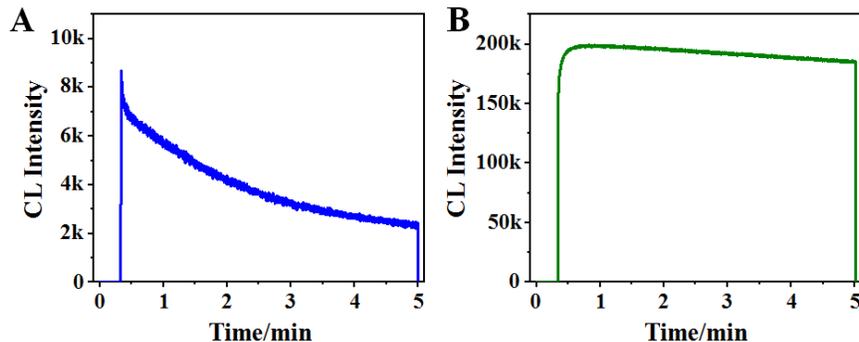


Figure 2. CL signals of the luminol- Co^{2+} - H_2O_2 system in the absence (A) and the presence (B) of C_8 -TPE- C_4 TAB.

CL enhancement in the presence of C_8 -TPE- C_4 TAB or conventional cationic surfactant. As

referred in previous work,³⁴ the CMC of C₈-TPE-C₄TAB was measured to be 46 μM. In this case, C₈-TPE-C₄TAB existed as the micelle but not monomer or dimer with 80 μM concentration. According to HRTEM measurement (Figure 3A), the formation of C₈-TPE-C₄TAB micelle (~6.2 nm, 100 counts) was observed. These results demonstrated that the enhanced CL was attributed to the C₈-TPE-C₄TAB micelle-promoted CL reaction. To understand the differences of C₈-TPE-C₄TAB micelle and typical ternary ammonium micelle promoted CL, the CL signals of luminol-Co²⁺-H₂O₂ system upon adding C₈-TPE-C₄TAB and cetyltrimethylammonium bromide (CTAB) were measured. The CMC of CTAB is reported to be 1.0 mM, and thus 2.0 mM CTAB was added to ensure the formation of CTAB micelle.³⁷ The HRTEM results indicated the formation of micelle with 2.0 mM CTAB (Figure S4). As shown in Figure 3B, the addition of CTAB largely enhanced the CL signals, indicating the universality of micelle-promoted CL. However, the CTAB-induced CL enhancement was lower than that of C₈-TPE-C₄TAB. Since the CTAB concentration is much higher than that of C₈-TPE-C₄TAB, the CTAB-induced CL enhancement may depend on its concentration. To understand the concentration effect, the CL signal of luminol-Co²⁺-H₂O₂ system were recorded upon adding CTAB with the different concentrations. As manifested in Figure 3C, the CL signals gradually increased with an increase in CTAB concentration, and showed a sudden increment around CMC. Further higher concentrations didn't show dramatic increase of CL. Therefore, the CTAB concentration with 2-folds of CMC would be enough to afford the stable micelle conditions.

In order to further figure out the possible reasons of the different CL enhancement characters, the other conventional cationic surfactants were tested, including tetradecyltrimethylammonium bromide (TTAB), dodecyltrimethylammonium bromide (DTAB) and decyltrimethylammonium bromide (DeTAB). To guarantee the formation of corresponding micelle, the concentrations of these surfactants were set to be 2-folds of their CMCs.³⁸ The concentrations of TTAB, DTAB, and DeTAB were 8, 32, and 114 mM, respectively. It was seen that the micelle-improved CL signals increased with the increasing alkyl chain length of surfactants (Figure 3D). Upon the addition of cationic surfactants with short alkyl chain length, even with ultrahigh concentrations (>30 mM), the CL signals were much lower than that by adding C₈-TPE-C₄TAB (80 μM). These results suggested that C₈-TPE-C₄TAB was superior to conventional cationic surfactants on the CL improvement toward luminol-Co²⁺-H₂O₂ system.

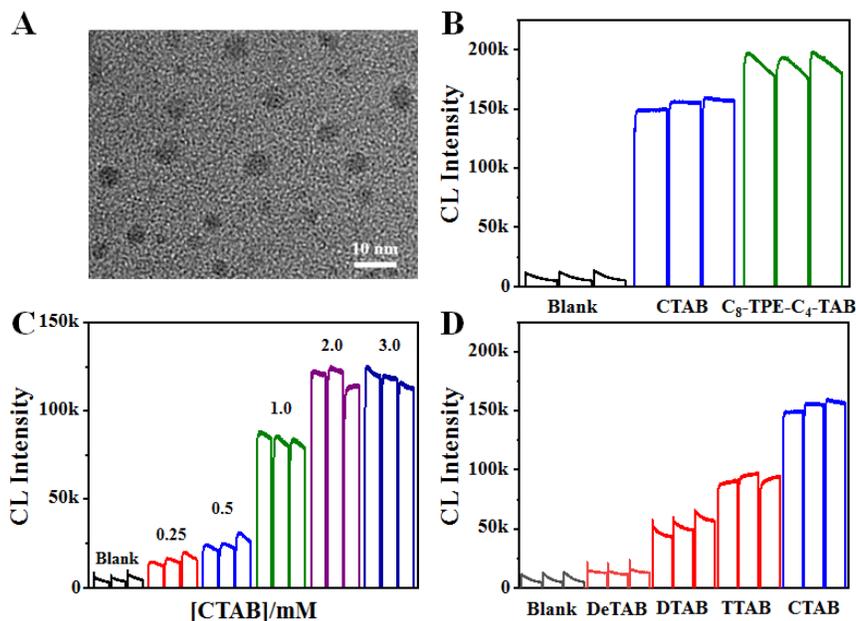


Figure 3. (A) HRTEM image of 80 μM C₈-TPE-C₄TAB. (B) CL signals of the luminol-Co²⁺-H₂O₂ system upon adding CTAB and C₈-TPE-C₄TAB. (C) CL signals of the luminol-Co²⁺-H₂O₂ system upon adding

CTAB with the different concentrations. (D) CL signals of the luminol- Co^{2+} - H_2O_2 system upon adding conventional cationic surfactants.

Mechanism of C_8 -TPE- C_4 TAB-mediated intensive and long-lasting CL emissions. As indicated above, the addition of C_8 -TPE- C_4 TAB endowed more effective CL reaction than conventional cationic surfactants. It is reported that cationic micelle can adsorb anionic reactants and benefit the CL reaction.³⁹ At pH 7.4, the C_8 -TPE- C_4 TAB micelle was positively charged (+11.0 mV) because of the outside tertiary ammonium cation (Figure S5), while luminol was negatively charged (-4.8 mV). The electrostatic attraction between positively charged C_8 -TPE- C_4 TAB micelle and negatively charged luminol dianion/peroxide anion easily leads to surface adsorption and enrichment of reactants.⁴⁰⁻⁴² Such an electrostatic attraction-assisted CL emission was also provided by SDS (sodium dodecyl sulfonate, a kind of typical anionic surfactant). As shown in Figure S6, the CL intensity of luminol- Co^{2+} - H_2O_2 system distinctly decreased upon adding SDS. This is because the outside sulfonic acid groups make SDS micelle negatively charged, which possesses strong electrostatic repulsion toward luminol dianion and peroxide anion.²⁰

To further understand the mechanism of C_8 -TPE- C_4 TAB-enhanced CL intensity and long-lasting emission, a few characterizations were performed. The generation of reactive oxygen species (ROS) is important to the CL signals. We tested the CL inhibition with the addition of different ROS scavengers. As displayed in Figure S7, *p*-benzoquinone (HQ) and thiourea caused visible CL suppression, while NaN_3 induced slight CL decrease, suggesting the primary ROS were superoxide radical ($\text{O}_2^{\bullet-}$) and hydroxyl radical ($^{\bullet}\text{OH}$).^{43,44} The electron paramagnetic resonance results also demonstrated the continuous generation of $\text{O}_2^{\bullet-}$ and $^{\bullet}\text{OH}$ during the CL reaction (Figure 4). It is reported that many ROS possess longer lifetime in hydrophobic environment.⁴⁵ When inserting TPE into the backbone of surfactant in this work, the hydrophobicity of alkyl chain increased, this might benefit the stabilization of ROS and promote the CL reaction.

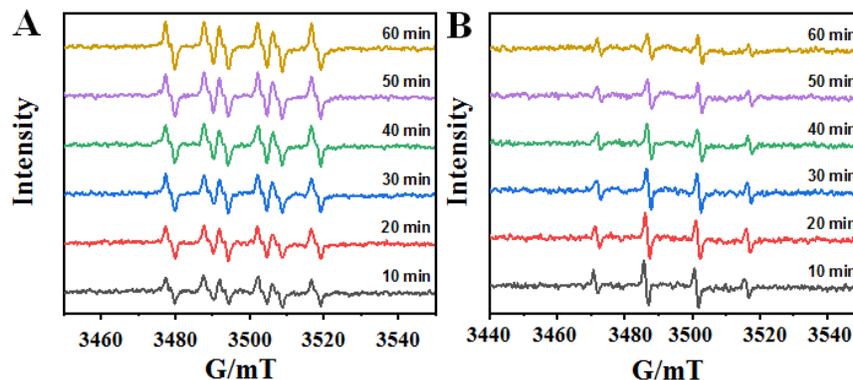


Figure 4. Time-dependent EPR spectra of the luminol- Co^{2+} - H_2O_2 - C_8 -TPE- C_4 TAB system.

As mentioned in CTAB concentration study, the formation of micelle plays important role in enhancing the CL emission. Thus, the total micelle number would affect the CL reaction. That is, less micelle leads to the high concentrations of reactants on the surface of micelle, and promotes the CL emission. In contrast, the average surface concentrations of reactants decreased with the increasing total micelle number. In this case, the CL reaction was inhibited and only weak CL emission could be observed. For C_8 -TPE- C_4 TAB and CTAB improved luminol- Co^{2+} - H_2O_2 systems, the final concentration of C_8 -TPE- C_4 TAB and CTAB were 80 μM and 2.0 mM, respectively. The aggregation number of micelle was calculated to be 64 in CTAB micelle, while it became 36 in C_8 -TPE- C_4 TAB micelle.⁴⁶ The total micelle numbers of CTAB micelle and C_8 -TPE- C_4 TAB micelle were determined to be 3.8×10^{15} and 2.3×10^{14} , respectively. The CTAB micelle number was 16-folds higher than that of C_8 -TPE- C_4 TAB micelle. Obviously, a single C_8 -TPE- C_4 TAB micelle surface exist more luminol dianion and peroxide anion, which contributes the higher CL signals.

In addition to high enrichment effect, CRET is also needed be considered in the CL enhancement of C₈-TPE-C₄TAB. The TPE fluorophore of C₈-TPE-C₄TAB could act as the CRET acceptor, and its AIE characters could avoid the luminescence quenching during the formation of micelle.^{47,48} In contrast, CTAB in the absence of intrinsic fluorophore could not act as the CRET acceptor. Then, the CL emission spectra of luminol-Co²⁺-H₂O₂ system with the addition of CTAB or C₈-TPE-C₄TAB were obtained. As shown in Figure 5A, the emission maximum of luminol-Co²⁺-H₂O₂ system located at 425 nm upon adding CTAB. The 425 nm light belongs to the excited luminol radicals.⁴⁹ However, the emission maximum shifted to 486 nm in the presence of C₈-TPE-C₄TAB (Figure 5B) and the CL emission spectrum was overlapped with the fluorescence emission profile of C₈-TPE-C₄TAB. The shifted emission maximum and characterized CL spectrum implied the occurrence of CRET in luminol-Co²⁺-H₂O₂-C₈-TPE-C₄TAB system.^{50,51} To determine the CRET efficiency (φ), the integral areas of emission of TPE acceptor (denoted as I_A) and total system (denoted as I_T) were acquired by peak fitting analysis. Based on the equation: $\varphi = I_A / I_T$, the φ was calculated to be 94.0%. As a result, the high enrichment and CRET contributed the intensive CL of luminol-Co²⁺-H₂O₂-C₈-TPE-C₄TAB system. The schematic illustration of C₈-TPE-C₄TAB micelle-amplified CL was displayed in Figure 6.

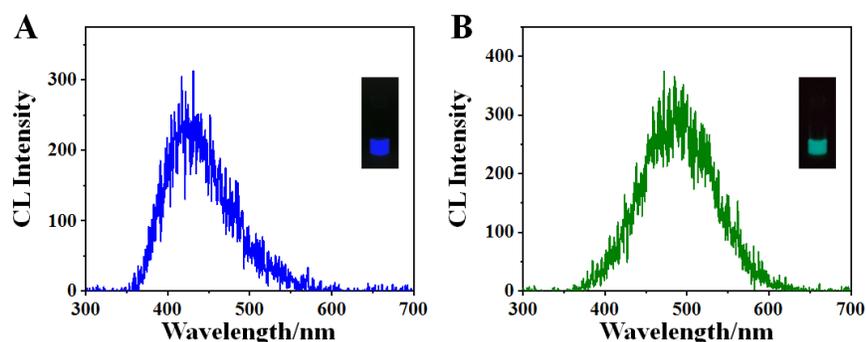


Figure 5. CL emission spectra of the luminol-Co²⁺-H₂O₂ system in the presence of CTAB micelle (A) and C₈-TPE-C₄TAB micelle (B). Inset pictures are the corresponding photographs.

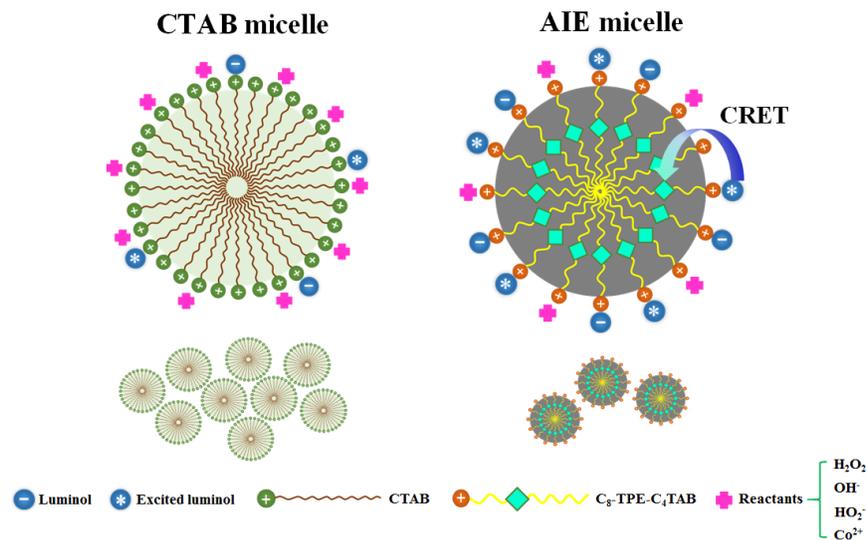


Figure 6. Schematic illustration of CTAB micelle (left) and C₈-TPE-C₄TAB micelle (right) amplified CL of the luminol-Co²⁺-H₂O₂ system.

To understand whether the insert location affected the CL emission, the CL signals of luminol-Co²⁺-H₂O₂ system upon adding C₄-TPE-C₈TAB (8th cationic headgroup insert), and TPE-C₁₂TAB (12th cationic headgroup insert) were recorded. As shown in Figure S8A, the CL intensity decreased as the extended insert location. A possible reason was due to the decreased CRET efficiency because the distance between excited luminol and TPE increases with the extended insert location (Figure S8B). The raised distance increased the energy loss and then decreased the CRET efficiency. Accordingly, all subsequent CL experiments were conducted with C₈-TPE-C₄TAB.

It is reported that the pH distribution in CTAB micelle solution is not uniform because of the adsorption of hydroxyl anions around the outside ternary ammonium cation layer.²⁰ Therefore, the local pH around micelle surface is slightly higher than that in solution. As is known, luminol could emit the strong CL under alkaline environment.⁵² To understand whether the surface adsorption hydroxyl anions affect the CL reaction, the CL signals of luminol-Co²⁺-H₂O₂-C₈-TPE-C₄TAB system without and with the introduction of NaBr or NaCl were investigated. As shown in Figure S9, the CL intensity decreased upon adding 1.0 mM Br⁻ or Cl⁻. The addition of Br⁻ or Cl⁻ would squeeze out the adsorbed hydroxyl anions, decreasing the pH around micelle surface and inhibiting the CL reaction. Such a result was also observed in CTAB-modified montmorillonite improved CL system, the removal of halide counterions of CTAB layer had a positive effect on the CL amplification.⁵³

It should be noticed that the acidity of H₂O₂ is very weak (pK_a ~11.7), that means the molar fraction of peroxide anion form increases with an increase in pH. However, under pH 7.4, the molar fraction of peroxide anion form was calculated to be 5.0 × 10⁻⁵, suggesting most H₂O₂ exists as neutral molecule form. This is why luminol-Co²⁺-H₂O₂ system only produces ultraweak CL emission. After the addition of C₈-TPE-C₄TAB, the adsorbed peroxide anions increased the local pH, which benefits the following CL reaction, and the consumed peroxide anions would be supplied by aqueous H₂O₂. The pH-dependent molar fractions of peroxide species were calculated and listed in Table S1. In a word, the non-uniform pH distribution may impel the diffusion of H₂O₂ from solution to micelle surface. However, the reaction rate was still slow due to the low molar fraction of peroxide anions. Interestingly, this process endows slow CL kinetics and long-lasting CL emission characters of luminol-Co²⁺-H₂O₂ system. On the other hand, the addition of surfactant also increased the viscosity of solution. The increased viscosity inhibited the diffusion of peroxide anions and limited the following CL reaction. To verify the viscosity-mediated CL performances, the CL signals of luminol-Co²⁺-H₂O₂ system were investigated in the absence and presence of glycerol. The CL kinetics became slow as the introduction of glycerol, as shown in Figure S10. These results demonstrated that C₈-TPE-C₄TAB-induced long-lasting CL emission might be attributed to the increased viscosity and the decreased fusion of reactants. Taken together, C₈-TPE-C₄TAB-mediated intensive and long-lasting CL emission is due to the synergistic effect of micelle-improved enrichment, the diffusion control of reactants and high-efficient CRET.

Long-lasting performances of the proposed CL system. To perform the long-lasting emission more clearly, the CL images were taken in real time by camera. For acquiring effective images, the concentrations of luminol, Co²⁺, H₂O₂, and C₈-TPE-C₄TAB were 60 μM, 10 nM, 2.5 mM, and 80 μM, respectively. The image was acquired with an interval of 4 min. Since the reaction occurs quickly, the 0 min point was not obtained; we herein provided the 0.5 min image as the first picture. As shown in Figure 7, bright blue emission was easily observed after the mixing of all CL substrates. Interestingly, there was no visible light attenuation even after 16 min reaction (Figure S11), suggesting this luminol-Co²⁺-H₂O₂-C₈-TPE-C₄TAB system was stable. Despite of the gradually decreased emission with the increasing reaction time, the CL emission was still observed after 60 min reaction. These results further verified the feasibility of the enhancement of intensive and long-lasting luminol CL by adding C₈-TPE-C₄TAB. The bright and long-lasting CL emission makes the luminol-Co²⁺-H₂O₂-C₈-TPE-C₄TAB system possible to construct a facile cold light for practical applications.

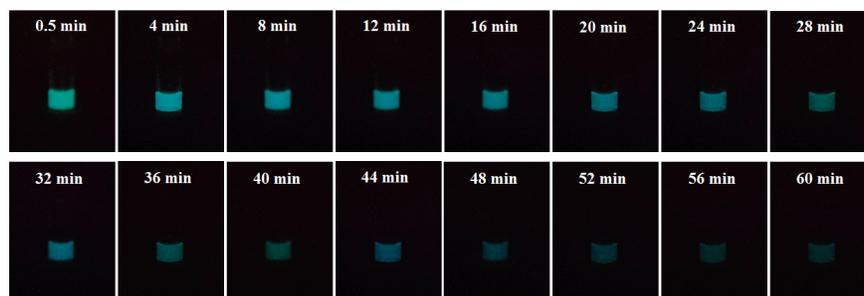


Figure 7. Time-dependent image of the luminol- Co^{2+} - H_2O_2 - C_8 -TPE- C_4 TAB system solution with 4 min interval acquisition.

3. Conclusion

In summary, the intensive luminol- Co^{2+} - H_2O_2 system with long-lasting CL emission has been explored by introducing the C_8 -TPE- C_4 TAB AIE surfactant. The micelle-improved enrichment and diffusion control of reactants and CRET were critical to amplify the CL signals. The visible CL emissions can be observed even after 60 min reaction at pH 7.4. This work not only develops a simple and glow-type luminol CL system, but also provides a general tactic to construct the novel surfactant-mediated CL system by introducing AIE surfactant with ultralow CMC, which reduces the usage of surfactant and environmental pollution. Moreover, our work also provides a deep learning of the relationship between CMC and surfactant-improved CL signals. Therefore, we believe this strategy might benefit the exploration of green and effective CL systems for lighting, optical sensing and photocatalysis applications, *etc.*

Acknowledgements

This work was supported by the National Natural Science Foundation of China (U22A20397, 21974008 and 22074005), the Natural Science Foundation of Beijing Municipality (2202038).

Conflict of Interests

The authors declare no competing financial interest.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Received: ((will be filled in by the editorial staff)) Revised: ((will be filled in by the editorial staff)) Published online: ((will be filled in by the editorial staff))

References

1. Z. Wang, J. Huang, J. Huang, B. Yu, K. Pu, F. J. Xu, *Aggregate* 2021, 2, e140.
2. S. Gnam, A. Scomparin, S. Das, R. Blau, R. Satchi-Fainaro, D. Shabat, *Angew. Chem. Int. Ed.* 2018, 57, 9033-9037.
3. H. Wu, M. Zhao, J. Li, X. Zhou, T. Yang, D. Zhao, P. Liu, H. Ju, W. Cheng, S. Ding, *ACS Appl. Mater. Interfaces* 2020, 12, 47270-47277.
4. P. Dang, X. Liu, H. Ju, J. Wu, *Anal. Chem.* 2020, 92, 5517-5523.
5. X. Teng, F. Li, C. Lu, B. Li, *Nanoscale Horiz.* 2020, 5, 978-985.
6. Z. Xiao, Y. Wang, B. Xu, S. Du, W. Fan, D. Cao, Y. Deng, L. Zhang, L. Wang, D. Sun, *Adv. Sci.* 2020, 7, 2000065.
7. Q. Song, X. Yan, H. Cui, M. Ma, *ACS Nano* 2020, 14, 3696-3702.
8. X. Chen, X. Wang, Y. Fang, L. Zhang, M. Zhao, Y. Liu, *Anal. Chem.* 2022, 94, 8382-8391.
9. W. Zhou, Y. Cao, D. Sui, C. Lu, *Anal. Chem.* 2016, 88, 2659-2665.
10. S. Dong, Z. Yuan, L. Zhang, Y. Lin, C. Lu,

Anal. Chem. 2017, 89, 12520-12526. 11. C. A. Marquette, L. J. Blum, Anal. Bioanal. Chem. 2006, 385, 546-554. 12. Y. Liu, W. Shen, Q. Li, J. Shu, L. Gao, M. Ma, W. Wang, H. Cui, Nat. Commun. 2017, 8. 13. Z. Li, L. Wang, Z. Yuan, C. Lu, Chem. Commun. 2019, 55, 679-682. 14. S. Chen, G. Yan, M. A. Schwartz, J. Perrin, S. Schulman, J. Pharm. Sci. 1991, 80, 1017-1019. 15. C. Zhang, J. Jin, K. Liu, X. Ma, X. Zhang, Chin. Chem. Lett. 2021, 32, 3931-3935. 16. G. Z. Tsogas, D. L. Giokas, A. G. Vlessidis, Anal. Chem. 2014, 86, 3484-3492. 17. A. Natrajan, D. Sharpe, D. Wen, Org. Biomol. Chem. 2011, 9, 5092-5103. 18. M. Xie, Z. Zhang, W. Guan, W. Zhou, C. Lu, Anal. Chem. 2019, 91, 2652-2658. 19. B. Factor, B. Muegge, S. Workman, E. Bolton, J. Bos, M. M. Richter, Anal. Chem. 2001, 73, 4621-4624. 20. W. L. Hinze, T. E. Reihl, H. N. Singh, Y. Baba, Anal. Chem. 1984, 56, 2180-2191. 21. M. Štěpánek, K. Podhájecká, K. Procházka, Y. Teng, S. E. Webber, Langmuir 1999, 15, 4185-4193. 22. X. Cai, B. Liu, Angew. Chem. Int. Ed. 2020, 59, 9868-9886.

23. L. Biesen, N. Nirmalanathan-Budau, K. Hoffmann, U. Resch-Genger, T. J. J. Müller, Angew. Chem. Int. Ed. 2020, 59, 10037-10041.

24. H. Liu, Z. Hu, H. Zhang, Q. Li, K. Lou, X. Ji, Angew. Chem. Int. Ed. 2022, 61, e202203505.

25. J. Chen, L. Mao, Y. Jiang, H. Liu, X. Wang, L. Meng, Q. Du, J. Han, L. He, H. Huang, Y. Wang, C. Xiong, Y. Wei, Z. Nie, ACS Nano 2023, DOI: 10.1021/acsnano.2c10058.

26. Z. Zhao, H. Zhang, J. W. Y. Lam, B. Z. Tang, Angew. Chem. Int. Ed. 2020, 59, 9888-9907. 27. J. Qian, B. Z. Tang, Chem 2017, 3, 56-91. 28. J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, Chem. Rev. 2015, 115, 11718-11940. 29. W. Guan, W. Zhou, C. Lu, B. Z. Tang, Angew. Chem. Int. Ed. 2015, 54, 15160-15164. 30. W. Guan, T. Yang, C. Lu, Angew. Chem. Int. Ed. 2020, 59, 12800-12805. 31. W. Guan, S. Wang, C. Lu, B. Z. Tang, Nat. Commun. 2016, 7, 11811. 32. J. Zhong, W. Guan, C. Lu, Green Chem. 2018, 20, 2290-2298.

33. Y. Liu, X. Chen, X. Liu, W. Guan, C. Lu, Chem. Soc. Rev. 2023, 52, 1456-1490. 34. J. Lou, X. Tang, H. Zhang, W. Guan, C. Lu, Angew. Chem. Int. Ed. 2021, 60, 13029-13034. 35. F. Pan, L. Liu, S. Dong, C. Lu, Spectrochim. Acta A 2014, 128, 393-397. 36. M. Wada, K. Abe, R. Ikeda, S. Harada, N. Kuroda, K. Nakashima, Talanta 2010, 81, 1133-1136. 37. M. Bielawska, A. Chodzińska, B. Jańczuk, A. Zdziennicka, Colloid Surf. A 2013, 424, 81-88. 38. T. Toshihiro, E. Satoshi, I. Hiroaki, Bull. Chem. Soc. Jpn. 1991, 64, 942-948.

39. Y. Yu, W. Guan, Z. Yuan, C. Lu, Anal. Methods 2022, 14, 1671-1677.

40. Z. Wang, X. Teng, C. Lu, Anal. Chem. 2015, 87, 3412-3418. 41. J. Zhong, Z. Yuan, C. Lu, Anal. Bioanal. Chem. 2016, 408, 8731-8746. 42. Y. Wang,; P. L. Dubin, H. Zhang, Langmuir 2001, 17, 1670-1673. 43. Y. Huang, R. Xie, K. Li, R. Tian, Y. Lin, C. Lu, ACS Appl. Mater. Interfaces 2023, 15, 1610-1618. 44. R. Zou, R. Xie, Y. Peng, W. Guan, Y. Lin, C. Lu, Anal. Chem. 2022, 94, 4813-4820. 45. S. Dong, J. Zhong, C. Lu, Anal. Chem. 2014, 86, 7947-7953.

46. R. G. Alargova, I. I. Kochijashky, M. L. Sierra, R. Zana, Langmuir 1998, 14, 5412-5418. 47. J. Chen; H. Qiu, S. Zhao, TrAC, Trends Anal. Chem. 2020, 122, 115747. 48. Y. Yan, X. Y. Wang, X. Hai, W. Song, C. Ding, J. Cao, S. Bi, TrAC, Trends Anal. Chem. 2020, 123, 115755. 49. Z. Li, D. Wang, Z. Yuan, C. Lu, Anal. Bioanal. Chem. 2016, 408, 8779-8786. 50. L. Zhang, M. Shi, W. Zhou, W. Guan, C. Lu, Anal. Chem. 2021, 93, 7724-7731. 51. L. Zhang, N. He, C. Lu, Anal. Chem. 2015, 87, 1351-1357. 52. R. Yang, Y. Ren, W. Dong, J. Mater. Chem. B 2023, 11, 1320-1330.

53. S. Chen, W. Zhou, Y. Cao, C. Xue, C. Lu, J. Phys. Chem. C 2014, 118, 2851-2856.

C₈-TPE-C₄TAB micelle mediated intensive and long-lasting CL of luminol-H₂O₂-Co²⁺ system with ultralow CMC.

Keywords: long-lasting chemiluminescence, fluorescent surfactant, aggregation-induced emission,

Youkai Yu,¹ Zhiqin Yuan^{*,2} and Chao Lu^{*,1,2}

¹ Y. Yu, Dr. Z. Yuan and Prof. Dr. C. Lu State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China

E-mail: yuanzq@mail.buct.edu.cn (Z. Yuan), luchao@mail.buct.edu.cn (C. Lu). Phone/Fax: +86 10 64411957.

² Prof. Dr. C. Lu Green Catalysis Center, and College of Chemistry, Zhengzhou University, Zhengzhou 450001, China

Long-Lasting Chemiluminescence by Aggregation-Induced Emission Surfactant with Ultralow Critical Micelle Concentration

