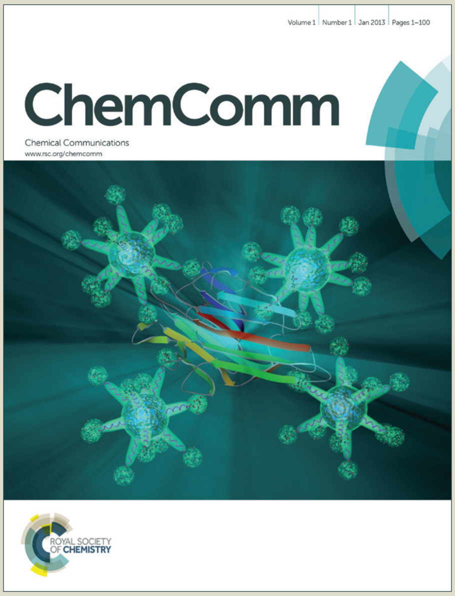
ChemComm

Accepted Manuscript



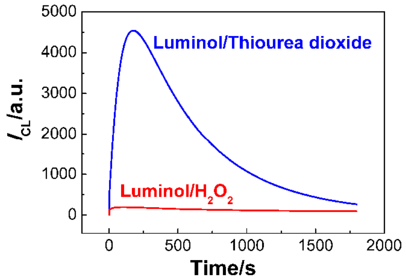
ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Table of contents entry:

Thiourea dioxide as unique eco-friendly coreactant of luminol chemiluminescence for sensitive detection of luminol, thiourea dioxide, and cobalt ions

Wenyue Gao, Wenjing Qi, Jianping Lai, Liming Qi, Saadat Majeed and Guobao Xu



Thiourea dioxide, a unique reductant that can generate oxygen upon decomposition, has been explored as efficient, cost-effective, and stable coreactant.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Thiourea dioxide as unique eco-friendly coreactant of luminol chemiluminescence for sensitive detection of luminol, thiourea dioxide, and cobalt ions

Wenyue Gao,[a,b] Wenjing Qi,[a,b] Jianping Lai,[a,b] Liming Qi,[a,b] Saadat Majeed[a,b] and Guobao Xu*[,a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Thiourea dioxide, a green industrial reductant, has been explored as efficient chemiluminescence coreactant for the first time. The luminol/thiourea dioxide chemiluminescence can be significantly enhanced by Co^{2+}. This system enables sensitive detection of thiourea dioxide, luminol, and Co^{2+}, particularly selective Co^{2+} detection.

Chemiluminescence (CL) is light-emitting phenomenon resulting from chemical reactions. Luminol is one of the most extensively investigated and used CL luminophores and continues to generate interest because of its low cost and broad applications.[1, 2] For example, luminol CL is the most frequently CL system for metal ion determination.[3-5] It is also one of the most popular CL systems for bioassays such as enzymatic biosensors,[6, 7] immunoassays,[8] aptasensors,[9, 10] DNA probe assays,[11, 12] and microarrays.[13, 14]

Oxidizing agents and activators are generally utilized to produce luminol CL.[1, 2] Typical oxidizing agents include hydrogen peroxide, oxygen, potassium permanganate, potassium dichromate, and hypochlorites.[15] Typical activators include peroxidase, catalase, cytochrome *c*, hemoglobin, deuterohemin, transition metal cations and transition metal complexes.[16] Since hydrogen peroxide and oxygen not only participate in many enzymatic reactions, but also can react with many substances, most luminol CL have been studied in the presence of hydrogen peroxide and oxygen.[4] However the easy reactions of hydrogen peroxide with numerous transition metal cations and transition metal complexes as well as the presence of transition metal cations, transition metal complexes and dissolved oxygen in solutions result in the poor selectivity of most luminol CL methods and the instability of hydrogen peroxide. So it is an urgent need to develop new luminol CL systems, particularly new luminol CL systems with high selectivity and good stability.

Thiourea dioxide (TD), also called formamidine-sulfinic or aminoiminomethanesulfinic acid, is a well-known industrial reducing agent.[17, 18] It decomposes in alkaline conditions to generate a strong reductant sulfoxylate which is then oxidized to yield a common biochemical reductant dithionite.[19] Because of its eco-friendly nature, low cost, and good stability, it has vast applications in paper, textile, and leather-processing industries for a long time.[20, 21] Recently, it has been used for the recycling and separation of precious metal. It has also been used for (1) the deoxygenation of α, β-epoxy ketones[22] and heteroatomic N-oxides, (2) the reduction of ketones,[23] quinones, nitrite, carbon dioxide, methyl viologen, aromatic nitro-, azoxy-, azo-, hydrazo- and organosulfur compounds,[24] (3) the oxidation of sulfides[25] and (4) the hydrolysis of imines in synthetic chemistry.[26] A unique property of this reductant and antioxidant is that TD can also generate oxygen.[19, 27] It implies that TD may react with luminol to generate CL.

In this study, a highly efficient CL of luminol/TD has been reported for the first time. TD can react with luminol to produce strong CL signals in the absence of any other activators. The luminol/TD system was used to detect luminol, TD and Co^{2+} with excellent sensitivity. The effects of oxygen and metal ions on CL of luminol/TD were studied. The luminol/TD system is not affected by oxygen and show excellent selectivity for Co^{2+} detection against many metal ions.

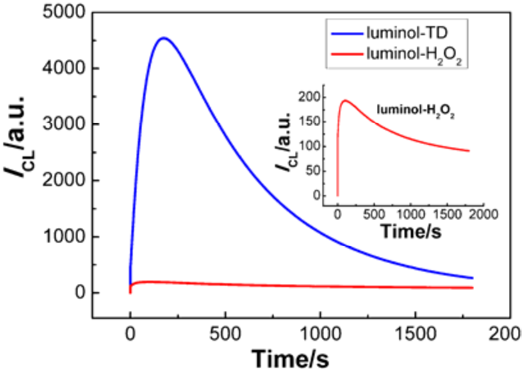


Fig. 1 The CL intensity-time curves of luminol/H_2O_2 (red line) and luminol/TD systems (blue line). Inset: Enlarged CL intensity-time curve of luminol/H_2O_2. c(luminol): 0.1 mM; c(TD): 1 mM; c(H_2O_2): 1 mM; photomultiplier tube voltage: 700 V.

Fig. 1 shows the CL intensity-time curves of luminol/TD system and luminol/H_2O_2 system. By comparison, the CL peak intensity of luminol/TD system is about 23 times higher than that of luminol/H_2O_2 system. It indicates that TD is an effective coreactant for luminol CL. As shown in Fig. S1, the maximum CL emission wavelength is about 450 nm, consistent with the typical spectrum of luminol.[28] It has been reported that TD can tautamerize and liberate oxygen in aqueous solutions (eq. 1 in Scheme 1).[19] Since oxygen can react with luminol to generate CL under some conditions,[1, 29] the effect of oxygen on the luminol/TD CL system has been investigated. As shown in Fig. 2, oxygen has negligible effect on the CL intensity of the luminol/TD system. It is particularly advantageous for CL detection to avoid the interference from oxygen. It also demonstrates that oxygen plays little role on the generation of CL of the luminol/TD system. Therefore, the hyproperoxide intermediate (compound A in eq. 1) generated from the decomposition of TD in alkaline solutions may oxidize luminol efficiently to produce strong CL as shown in eq. 2 of Scheme 1.

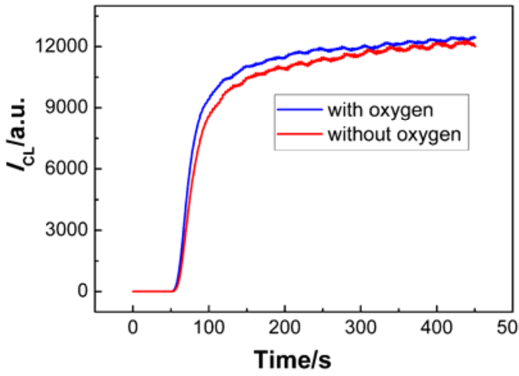
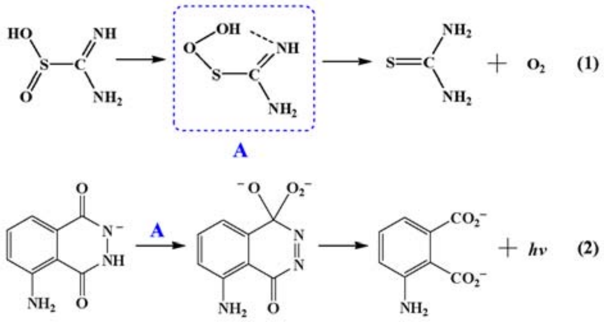


Fig. 2 The CL intensity-time curves in the absence (red line) and presence (blue line) of oxygen. c(luminol): 0.1 mM; c(TD): 10 mM; photomultiplier tube voltage: 700 V. Luminol solutions and TD solutions were deoxygenated with nitrogen for half an hour.



Scheme 1 Reaction mechanism for the luminol/TD CL system.

Fig. 3 shows the effects of pH on CL intensities. The CL intensities increase with increasing pH from 10.3 to 11.9, and then decrease as pH increase further. The increase in CL intensities with increasing pH from 10.3 to 11.9 are attributed to the faster generation of effective hyproperoxide intermediates from TD at higher pH and the deprotonation of luminol. When the pH becomes higher than 12, the decomposition of TD may generate much strong reductants, sulfoxylate and dithionite. The as-generated strong reductants may consume hyproperoxide intermediates, resulting in the decrease in CL intensities.[20]

This system was used to detect TD and luminol. The CL intensities have a good linear relationship with TD concentrations from 2 to 1000 μM with correlation coefficient (r) of 0.9967 (Fig. S2). The linear equation is $I = -3.61 + 0.92\ c$ (μM). The limit of detection (LOD) for TD is calculated to be 1.03 μM. Compared with other methods,[30-32] this CL method is a sensitive, fast and simple method for the detection of TD. The method exhibits nice reproducibility with a relative standard deviation (RSD) of 4.27% for nine consecutive determinations of 1 mM TD. Moreover, the logarithm of CL intensity ($\log I$) has good linear relationship with logarithm of concentrations of luminol (logc) from 1 to 10^5 nM (Fig. S3). The linear equation is $\log I = 9.98 + 0.99 \log c$ (M) (r = 0.9986). The LOD is 0.95 nM, which is comparable to the best LOD of other reported luminol detection methods.[3] The RSD for nine consecutive measurements of 500 nM luminol is 3.39%.

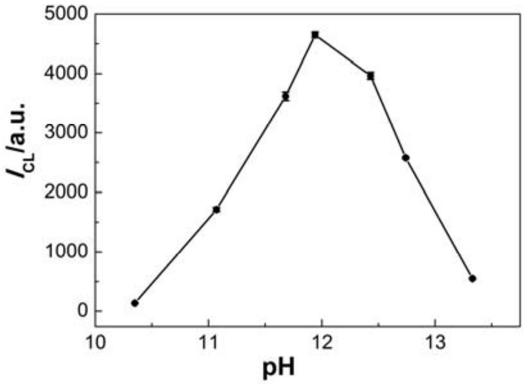


Fig. 3 pH effect on the CL intensities. c(luminol): 0.1 mM; c(TD): 10 mM; photomultiplier tube voltage: 700 V.

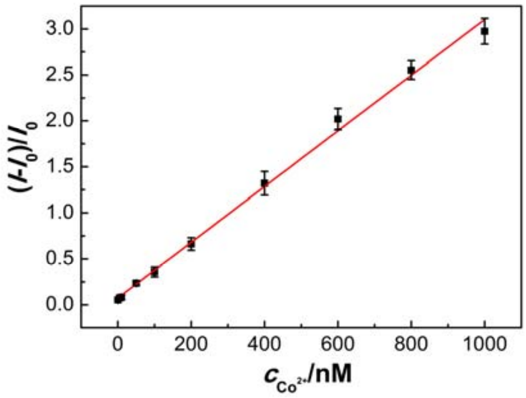


Fig. 4 Linear calibration curve of Co^{2+}. I represents CL intensity of the system after the addition of Co^{2+}; I_0 represents CL intensity of the control sample; $(I-I_0)/I_0$ represents CL enhancement efficiency after the addition of Co^{2+}. c(TD): 1 mM; c(luminol): 10 μM; c(Co^{2+}): 0.5, 5, 10, 50, 100, 200, 400, 600, 800, 1000 nM; photomultiplier tube voltage: 1000 V.

It is well-known that some transitional metal cations can promote luminol CL reactions to enhance the CL intensities.[3] It has also been reported that some cobalt chelates can catalyze some reactions of TD.[33, 34] Inspired by these studies, we investigated the effect of cobalt ion on the CL intensities of the luminol/TD system. The experiment results show that Co^{2+} can significantly increase the CL intensities of the luminol/TD system, which is then utilized to detect Co^{2+}. Fig. 4 shows the linear calibration curve of Co^{2+}. The CL enhancement efficiency of $(I-I_0)/I_0$ has linear relationship with the concentrations of Co^{2+} from 0.50 to 1000 nM with the linear equation of $(I-I_0)/I_0 = 0.074 + 0.0030c$ (nM) (r = 0.9980). The LOD is 0.20 nM. The RSD (n = 9) for the detection of 1μM Co^{2+} is 4.60%. In comparison with other reported CL Co^{2+} detection methods, our method is very sensitive and simple.[35-41]

The detection of metal ions by conventional luminol CL methods is easily interfered by other metal ions. It is thus desirable to develop method for selective detection. Therefore, the selectivity of the proposed method for the detection of Co^{2+} was investigated. As shown in Fig. 5, CL intensity increases dramatically in the presence of Co^{2+}. In contrast, CL intensities change negligibly in the presence of other metal ions. The results suggest that the Co^{2+} detection method based on the luminol/TD system has nice selectivity. The excellent selectivity is attributed to the unique interaction of Co^{2+} with TD since cobalt complexes are used as the catalysts in most synthesis using TD.[33, 34] The remarkable selectivity makes the luminol/TD system distinctive from other luminol systems that generally do not show good selectivity.[40]

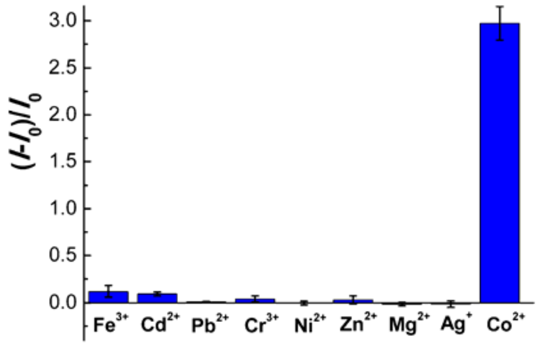


Fig. 5 Selectivity for the detection of Co^{2+}. I represents CL intensity of the system after the addition of metal ions; I_0 represents CL intensity of the control sample; $(I-I_0)/I_0$ represents CL enhancement efficiency after the addition of metal ions. The concentrations of all the metal ions are 1 µM. c(TD): 1 mM; c(luminol): 10 µM; photomultiplier tube voltage: 1000 V.

Conclusions

Luminol CL using an eco-friendly, stable, and cheap coreactant TD have been reported for the first time. The CL intensities of the luminol/TD system can be significantly enhanced by Co^{2+}. The newly-developed luminol/TD CL system enables the highly sensitive detection of luminol, TD, and Co^{2+}. Moreover, the luminol/TD CL system exhibit excellent selectivity for the detection of Co^{2+} against other transitional metal ions. The remarkable selectivity against other transitional metal ions makes the luminol/TD CL system attractive for broad applications. This study also indicates that TD is a promising coreactant for other CL systems.

Acknowledgements

This project was supported by the National Natural Science Foundation of China (No. 21175126), and Faculty Development Programm of Bahauddin Zakaryia University, Multan, Pakistan (100 Foreign Scholarships) (No.PF/Cont./2-50/Admin/5398).

[a] *State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, China. Fax: +86 431 85262747; Tel: +86 431 85262747; E-mail: guobaoxu@ciac.ac.cn*
[b] *University of the Chinese Academy of Sciences, Chinese Academy of Sciences, No. 19A Yuquanlu, Beijing 100049, PR China.*
**Corresponding author: Prof. G. B. Xu*

† Electronic Supplementary Information (ESI) available: Experimental details. See DOI: 10.1039/b000000x/

1. M. M. Richter, *Chem. Rev.* , 2008, **104**, 3003-3036.
2. L. Z. Hu and G. B. Xu, *Chem. Soc. Rev.* , 2010, **39**, 3275-3304.
3. S. J. Ussher, M. Yaqoob, E. P. Achterberg, A. Nabi and P. J. Worsfold, *Anal. Chem.* , 2005, **77**, 1971-1978.
4. G. Z. Tsogas, D. L. Giokas and A. G. Vlessidis, *Anal. Chem.*, 2014, **86**, 3484-3492.
5. S. Cai, K. M. Lao, C. Lau and J. Z. Lu, *Anal. Chem.* , 2011, **83**, 9702-9708.
6. C. A. Marquette and L. J. Blum, *Anal. Bioanal. Chem.*, 2006, **385**, 546-554.
7. A. Roda, E. Michelini, L. Cevenini, D. Calabria, M. M. Calabretta and P. Simoni, *Anal. Chem.*, 2014, **86**, 7299-7304.
8. T. S. Bailey and M. D. Pluth, *J. Am. Chem. Soc.*, 2013, **135**, 16697-16704.
9. S. Y. Li, D. Y. Chen, Q. T. Zhou, W. Wang, L. F. Gao, J. Jiang, H. J. Liang, Y. Z. Liu, G. L. Liang and H. Cui, *Anal. Chem.*, 2014, **86**, 5559-5566.
10. X. Q. Liu, R. Freeman, E. Golub and I. Willner, *ACS Nano*, 2011, **5**, 7648-7655.
11. Y. He, D. Q. Liu, X. Y. He and H. Cui, *Chem. Commun.*, 2011, **47**, 10692-10694.
12. Y. Gao and B. X. Li, *Anal. Chem.*, 2014, **86**, 8881-8887.
13. X. M. Chen, B. Y. Su, X. H. Song, Q. A. Chen, X. Chen and W. X. R., *TrAC Trend Anal. Chem.*, 2011, **30**, 665-676.
14. S. C. Donhauser, R. Niessner and M. Seidel, *Anal. Chem.*, 2011, **83**, 3153-3160.
15. P. Khan, D. Idrees, M. A. Moxley, J. A. Corbett, F. Ahmad, G. von Figura, W. S. Sly, A. Waheed and M. I. Hassan, *Appl. Biochem. Biotechnol.*, 2014, **173**, 333-355.
16. A. l. A. M. Santafé, B. Doumèche, L. J. Blum, A. s. P. Girard-Egrot and C. A. Marquette, *Analytical chemistry*, 2010, **82**, 2401-2404.
17. A. A. Cuadri, P. Partal, F. J. Navarro, M. Garcia-Morales and C. Gallegos, *Fuel*, 2011, **90**, 2294-2300.
18. S. Verma, S. Kumar, S. L. Jain and B. Sain, *Org. Biomol. Chem.*, 2011, **9**, 6943-6948.
19. Z. Kis, S. V. Makarov and R. Silaghi-Dumitrescu, *J. Sulfur Chem.*, 2010, **31**, 27-39.
20. L. Zhou, X. Y. Liu, J. Z. Shao and Y. N. Chen, *Adv. Mater. Res.*, 2012, **396-398**, 1174-1179.
21. S. V. Makarov, A. K. Horvath, R. Silaghi-Dumitrescu and Q. Y. Gao, *Chem. Eur. J.*, 2014, **20**, 1-14.
22. R. B. dos Santos, T. J. Brocksom and U. Brocksom, *Tetrahedron Lett.*, 1997, **38**, 745-748.
23. K. Nakagawa and K. Minami, *Tetrahedron Lett.*, 1972, **13**, 343-346.
24. C. Daneault and C. Leduc, *Cellul. Chem. Technol.*, 1994, **28**, 205-217.
25. S. Kumar, S. Verma, S. L. Jain and B. Sain, *Tetrahedron Lett.*, 2011, **52**, 3393-3396.
26. S. Kumar, S. L. Jain and B. Sain, *RSC Adv.*, 2012, **2**, 789-791.
27. E. M. Burgess, U. Zoller and J. R. L. Burger, *J. Am. Chem. Soc.*, 1984, **106**, 1128-1130.
28. E. H. White and M. M. Bursey, *J. Am. Chem. Soc.*, 1964, **86**, 941-942.
29. E. H. White, O. Zafiriou, H. H. Kagi and J. H. M. Hill, *J. Am. Chem. Soc.*, 1964, **86**, 940-941.
30. Z. X. Pan, *Chin. J. Anal. Chem.*, 1995, **23**, 732.
31. Z. X. Pan and J. Y. Zang, *Chin. J. Anal. Lab.*, 2007, **26**.
32. H. Wang, X. W. Zeng, X. T. Chang, X. K. Peng, L. X. Xia and Y. W. Li, *Chin. J. Chrom.*, 2014, **32**, 21-25.
33. A. S. Pogorelova, S. V. Makarov, E. S. Ageeva and R. Silagi-Dumitresku, *Kinet. Katal.* , 2009, **83**, 2050-2053.
34. E. A. Vlasova, S. V. Makarov and M. N. Malinkina, *Kinet. Katal.* , 2010, **84**, 573-577.
35. L. Feng, X. Li, H. Li, W. Yang, L. Chen and Y. F. Guan, *Anal. Chim. Acta*, 2013, **780**, 74-80.
36. D. Tsoutsi, L. Guerrini, J. M. Hermida-Ramon, V. Giannini, L. M. Liz-Marzan, A. Wei and R. A. Alvarez-Puebla, *Nanoscale*, 2013, **5**, 5841-5846.
37. S. Ghosh, U. Anand and S. Mukherjee, *Anal. Chem.*, 2014, **86**, 3188-3194.
38. Z. M. Liu, X. L. Jia, P. P. Bian and Z. F. Ma, *Analyst*, 2014, **139**, 585-588.
39. M. C. Talio, M. Alesso, M. G. Acosta, M. Acosta and L. P. Fernandez, *Talanta*, 2014, **127**, 244-249.

40. X. Y. Chen, C. Liu, Z. Xu, Y. Z. Pan, J. S. Liu and L. Q. Du, *Microsyst. Technol.*, 2012, **19**, 99-103.
41. J. X. Shi, C. Lu, D. Yan and L. N. Ma, *Biosens. Bioelectron.*, 2013, **45**, 58-64.