

EOSIN Y-SENSITIZED CHEMILUMINESCENCE OF 7,7,8,8-TETRACYANOQUINODIMETHANE
IN SURFACTANT VESICLES FOR DETERMINATION OF MANGANESE(II)
AT SUB-NANOGRAM LEVELS BY FLOW INJECTION METHOD

Masaaki YAMADA,* Satoru KAMIYAMA, and Shigetaka SUZUKI
Department of Industrial Chemistry, Faculty of Technology,
Tokyo Metropolitan University, Setagaya-ku, Tokyo 158

Luminous oxidation of 7,7,8,8-tetracyanoquinodimethane(TCNQ) by dissolved O_2 is utilized for sensitive determination of Mn(II). The weak chemiluminescence of TCNQ is effectively sensitized by eosin Y in didodecyldimethylammonium bromide bilayer vesicles. The limit of determination is 0.01 ng(20- μ l sample injection).

Analytical utility of surfactant aggregates like micelles which amphiphile molecules form in aqueous solution has currently been emphasized in chromatography and spectroscopy.¹⁾ Such organized assemblies exhibit many unique properties facilitating analytical measurements, e.g., solubilization, concentration and compartmentalization of reactants and/or analytes, alterations of microenvironment, chemical and photophysical pathways and rates, etc.²⁾ These properties are very attractive in the analytical use of solution chemiluminescence(CL) because there is much possibility of enhancing quantum efficiency or energy transfer efficiency, because they permit the use of CL reagents and sensitizers insoluble in water, and because they serve to improve selectivity. We already reported micelle-enhanced CL methods for highly selective determination of Cu(II) at sub-pg levels³⁾ and for direct continuous monitoring of SO_2 at ppb levels.⁴⁾ This letter demonstrates that a new CL system, TCNQ/ O_2 /NaOH, is reinforced by the addition of sensitizer and surfactant for sensitive determination of manganese(II) by flow injection method. TCNQ as a CL reagent is solubilized in organized assemblies which cationic surfactant molecules form. The weak CL arising from the Mn(II)-catalyzed oxidation of TCNQ by dissolved O_2 in alkaline solution is sensitized by eosin Y; the sensitized CL is further enhanced by means of bilayer vesicles which is different from micelles in structures as described later.

A schematic diagram of the flow system is given in Fig. 1. It is basically as previously described, except that there is no mixing coil.⁵⁾ The solubilization of TCNQ was done by sonication for ca.1 h.

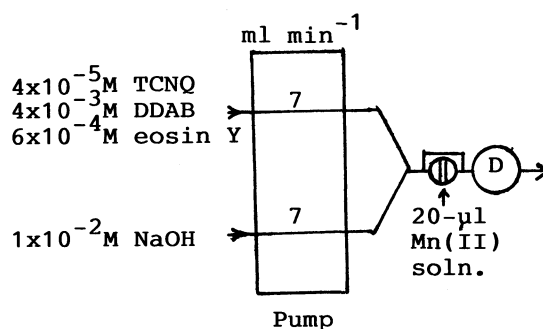


Fig. 1. Schematic diagram of the flow system.

Table 1. Effect of surfactant aggregates on the CL signal for Mn(II)^{a)}

Cationic surfactant	Concn ^{b)} /10 ⁻³ M	Relative CL signal Sensitizer		
		None	Fluorescein	Eosin Y
DTAB [C ₁₂ H ₂₅ N(CH ₃) ₃]Br	80 (16)	2.8		54
TTAB [C ₁₄ H ₂₉ N(CH ₃) ₃]Br	14 (3.5)	1.3	7.1	19
HTAB [C ₁₆ H ₃₃ N(CH ₃) ₃]Br	4 (0.9)	0.4	0.9	
OTAC [C ₁₈ H ₃₇ N(CH ₃) ₃]Cl	1.4(0.34)	0.4	0.2	
HEAB [C ₁₆ H ₃₃ (C ₂ H ₅)N(CH ₃) ₂]Br	20	0.2	7.1	36
DDAB [(C ₁₂ H ₂₅) ₂ N(CH ₃) ₂]Br	0.8(0.18)	1.0	21	260
HPC [C ₁₆ H ₃₃ NC ₅ H ₅]Cl	40 (0.9)	0.3	0.5	
TDBAC[C ₁₄ H ₂₉ (C ₆ H ₅ CH ₂)N(CH ₃) ₂]Cl	1.5(0.37)	1.4	0.8	

a) 5x10⁻⁵M TCNQ, 0.2M NaOH, 10⁻⁴M fluoresceine, 10⁻⁵M eosin Y, 10⁻³M Mn(II),
Flow rate =5 ml min⁻¹

b) The figures in parentheses show CMCs.

As not only TCNQ-solubilizers but also reaction media, various cationic surfactant aggregates were examined for sensitive detection of Mn(II). The results are shown in Table 1. In the absence of sensitizer, any organized assemblies did not yield strong Mn(II)-catalyzed CL. On the other hand, with some organized assemblies the CL signal was considerably enhanced by the presence of fluorescein in the CL system, the emission being sensitized by ca.21 times in the didodecyldimethylammonium bromide(DDAB) solution which was the best choice in reaction medium. Further enhanced CL signal was obtained by the substitution of eosin Y for fluorescein, the emission being sensitized by a factor of 260. It is known that surfactant molecules with two long-chain alkyl groups like DDAB form bilayer aggregates (vesicles) rather than micelles.⁶⁾ Such vesicular aggregates of the bilayer membrane exhibit higher organization, stability, and rigidity than micellar aggregates do, resulting in the occurrence of more effective energy transfer to the sensitizer.⁷⁾ This is the reason why the magnitude of sensitization is the largest in the DDAB solution. Anionic and nonionic micellar solutions and common organic solvents miscible in water did not surpass the DDAB solution with regard to the reaction medium.

The recommended conditions(as specified in Fig. 1) provided a logarithmic calibration graph with a slope of unity, a linear dynamic range of about 10³, and a limit of determination of 0.01 ng(20- μ l sample injection). For evaluation of the selectivity in the present CL system, various species were injected. Iron(II, III) and magnesium(II) gave relative molar CL signals 6 and 1 % of that for Mn(II), respectively, when 10⁻⁴M solution of each species was injected; no CL signal was observed when 10⁻⁵M solutions of these species were injected. Injections of 10⁻⁴ M solutions of other species like Co(II), Ni(II), Cu(II), Zn(II), Cr(III,VI), Pb(II), Cd(II), Ag(I), Mo(VI), Al(III), Ca(II), F⁻, Cl⁻, Br⁻, I⁻, CO₃²⁻, PO₄³⁻, SO₄²⁻, NO₃⁻, CH₃COO⁻, C₂O₄²⁻, and citric acid gave rise to no emission.

The following explanation is suggested for the Mn(II)-catalyzed CL reaction. TCNQ is a strong electron acceptor, as a result of the cumulative electron withdrawal

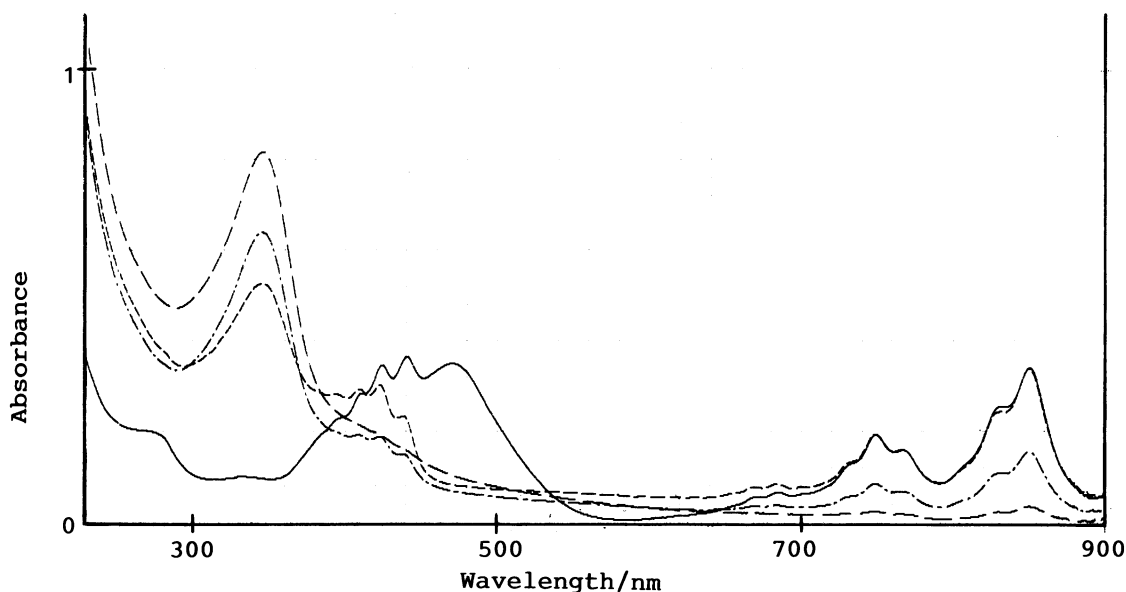
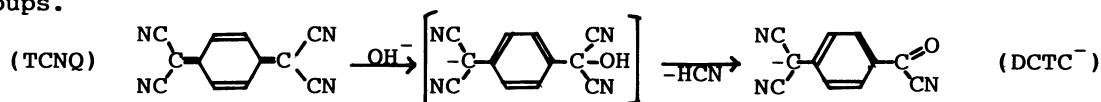


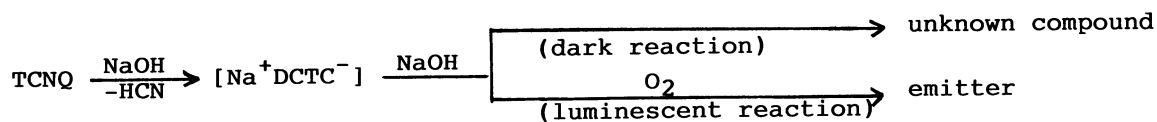
Fig. 2. Electronic absorption spectra in DDAB solution.

————: 1.3×10^{-5} M TCNQ; -----: 1.3×10^{-5} M TCNQ, 3×10^{-3} M NaOH; - · - · - · : 1.3×10^{-5} M TCNQ, 3×10^{-3} M NaOH, 3×10^{-6} M Mn(II); — — — : 1.3×10^{-5} M TCNQ, 3×10^{-3} M NaOH, 1.7×10^{-5} M Mn(II)

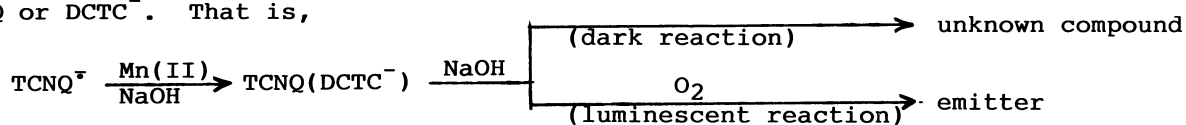
by the four CN groups. When TCNQ is solubilized in surfactant solutions above CMC, a remarkable coloration due to the formation of charge transfer complex between TCNQ and surfactant molecule is observed.⁸⁾ The electronic absorption spectrum of TCNQ solubilized in DDAB vesicular solution is shown in Fig. 2. The bands of about 420-440, 750, and 850 nm are characterized with TCNQ anion radical (TCNQ⁻).⁹⁾ The 470 nm band is caused by the charge transfer complex of TCNQ and/or a hydrolysis product of TCNQ, α, α -dicyano-p-toluoylecyanide (DCTC⁻) anion which is formed by the nucleophilic addition of OH⁻ on the carbon α of TCNQ, positively polarized by the presence of two CN groups.¹⁰⁾



The electronic absorption spectra of TCNQ solution after both the alkalification and the Mn(II)-catalyzed CL reaction are also illustrated in Fig. 2. The alkalification leads to the appearance of a new absorption band at ca. 345 nm (an unknown compound) in place of the disappearance of the 470 nm band, but does not affect the TCNQ⁻ bands. It is conceivable that in alkaline solution DCTC⁻ further reacts with dissolved O₂ to emit light which is the background CL in the present CL system. This was confirmed by the use of DCTC⁻ which was separately prepared from TCNQ and NO₂⁻ in aqueous acetone solution.¹¹⁾ That is to say, DCTC⁻ prepared exhibited absorption maxima at 280 and 470 nm and gave rise to CL on alkalification to form the unknown compound stated above. Both light emissions were not observed under deaerated conditions. In contrast, the unknown compound was formed by the alkalification of TCNQ solution regardless of the presence of dissolved O₂. From these findings, a reaction scheme involving a route of nonluminescent reaction can be proposed for the background CL. That is,



On the other hand, in the Mn(II)-catalyzed CL reaction the decrease in the TCNQ^- band intensity causes the appearance of the absorption band for the unknown compound; the changes in both band intensities depend on the Mn(II) concentration. This means that Mn(II) works catalytically on TCNQ^- in alkaline solution to yield the unknown compound. The Mn(II) catalyzed-CL signal was not observed under de-aerated conditions, whereas the unknown compound was formed from TCNQ^- regardless of the presence of dissolved O_2 . Accordingly, a reaction scheme similar to that for the background CL can be written for the Mn(II)-catalyzed CL. Considering that the substitution of DCTC^- for TCNQ in Fig. 1 resulted in no Mn(II)-catalyzed CL signal, the Mn(II)-catalyzed CL reaction may proceed via a route of the formation of TCNQ or DCTC^- . That is,



It is not obvious how Mn(II) participates in the formation reaction of $\text{TCNQ(DCTC}^-)$ and what the emitter is. However, we can say that the vesicular effect exerts favorably on the catalytic reaction and the luminescent reaction.

These preliminary results imply that Mn(II) at sub-ng levels can be determined selectively by means of the unique CL system with fewer interferences than any other CL system. The luminol system also permits the determination of Mn(II) at ng levels but the use of oxidizing agent (H_2O_2) causes interferences due to many transition metals.¹²⁾ There is room for further development of the present flow system; better characteristics should be achieved by the injection of Mn(II) solution into the TCNQ stream and by the mixing of two reagent streams inside a flow cell because the CL is emitted as soon as the Mn(II) solution is injected. This should provide increased sensitivity and reduced reagent-consumption due to lowered flow rates.

One of the authors(M.Y.) is gratefully acknowledged to Dr.Takehiko Suzuki (Lab. Ind. Org. Chem.) for helpful discussion.

References

- 1) E.Pelizzetti and E.Pramauero, *Anal.Chim.Acta*, **169**, 1(1985).
- 2) L.J.Cline love, J.G.Habarta, and J.G.Dorsey, *Anal.Chem.*, **56**, 1133A(1984).
- 3) M.Yamada and S.Suzuki, *Anal.Lett.*, **17**, 251(1984).
- 4) M.Kato, M.Yamada, and S.Suzuki, *Anal.Chem.*, **56**, 2529(1984).
- 5) M.Yamada, T.Nakada, and S.Suzuki, *Anal.Chim.Acta*, **147**, 401(1983).
- 6) T.Kunitake and Y.Okahata, *J.Am.Chem.Soc.*, **99**, 3860(1977) and subsequent papers.
- 7) J.Nikokavouras, G.Vassilopoulos, and C.M.Paleos, *J.Chem.Soc., Chem.Comm.*, **1981**, 1082.
- 8) S.Muto, K.Deguchi, K.Kobayashi, E.Kaneko, and K.Meguro, *J.Coll. and Interface Sci.*, **33**, 475(1970).
- 9) S.Muto, K.Deguchi, Y.Shimazaki, Y.Ando, and K.Meguro, *Bull.Chem.Soc.Jpn.*, **44**, 2087(1971).
- 10) M.Kryszewski, W.Ciesielski, and J.Pecherz, *Acta Polym.*, **32**, 524(1981).
- 11) W.R.Hertler, H.D.Hartzler, D.S.Acker, and R.E.Benson, *J.Am.Chem.Soc.*, **84**, 3387(1962).
- 12) J.L.Burguera and A.Townshend, *Talanta*, **28**, 731(1981).

(Received August 10, 1985)