Peroxyoxalate chemiluminescence enhanced by oligophenylenevinylene fluorophores in the presence of various surfactants

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Abstract: The effect of several surfactants on peroxyoxalate chemiluminescence (PO-CL) using oligophenylenevinylene fluorophores was investigated. Among several oligophenylenevinylenes consisting of some stilbene units, linearly conjugated ones, such as distyrylbenzene and distyrylstilbene, effectively enhanced PO-CL efficiency. Various effects of anionic, cationic, amphoteric and non-ionic surfactants on the CL efficiency of PO-CL were determined using three oxalates and the distyrylbenzene fluorophore. Anionic and non-ionic surfactants effectively enhanced CL efficiency, in contrast to the negative effect of cationic and amphoteric surfactants. Non-ionic surfactants were also effective in CL reactions of oxalates bearing dodecyl ester groups by the hydrophobic interaction between their alkyl chains. Considering these results, the surfactants not only increase the concentrations of water-insoluble interacting species in the hydrophobic micelle cores, but also control rapid degradation of the oxalates by alkaline hydrolysis.

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Introduction

Peroxyoxalate chemiluminescence (PO-CL), the most effective of the various chemiluminescence (CL) systems (1), has received much attention since its discovery (2). PO-CL can be readily carried out by the reaction of active oxalates, such as bis(2,4,6-trichlorophenyl) oxalate (TCPO) or bis(2,4-dinitrophenyl) oxalate (DNPO), as luminophores and hydrogen peroxide in the presence of various types of fluorophores. Because of its practical simplicity and high efficiency, PO-CL is not

only used as a chemical light source, but is also comprehensively applied to analytical chemistry. A wide variety of chemical and biological analytes can be both qualitatively and quantitatively determined using these CL systems as signals of light emission (3,4). However, there are some problems with this CL system, namely, both oxalates and fluorophores are generally insoluble in aqueous media and active oxalates are unstable in aqueous conditions; PO-CL reactions are generally performed in aqueous media due to the use of aqueous hydrogen peroxide as an oxidizing agent. In addition, hydrophobic environments are favorable for the chemiexcitation step in which the hydrophobic fluorophores and high-energy intermediates such as 4-aryloxy-4-hydroxy-1,2-dioxetane-3-ones or 1,2-dioxetane-3,4-dione interact. An effort to improve these deficiencies has been made using some water-soluble oxamides (5), but they have not been used in practice. Another simple method is the use of surfactants, which lead to changes in the microenvironments in which reactive intermediates take part in the chemiexcitation steps by interacting with the fluorophores. Several reports have dealt with the effects of surfactants on PO-CL, and various effects of neutral, cationic and anionic surfactants on the CL efficiency have been documented (6–14), however, these results cannot be easily integrated into a simple system because surfactants behave in different ways depending on the reactants and the reaction conditions.

By contrast, many aromatic fluorophores have been used for PO-CL, and we have shown that 1,4-distyrylbenzenes are very useful in PO-CL systems because of their strong fluorescence, controllable emission wavelength and synthetic availability (15–17). Because distyrylbenzene is one of the oligophenylenevinylenes useful as a fluorescent material for optoelectronic and photonic devices (18,19), it is interesting to use some low molecular mass oligophenylenevinylenes as fluorophores for PO-CL systems.

Here, we report the preparation and physical properties of some fluorescent oligophenylenevinylenes consisting of some stilbene units, and their use in a PO-CL system with three oxalates. In addition, the effects of various anionic, cationic, amphoteric and non-ionic surfactants on the CL efficiency are reported.

Experimental

Apparatus

^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were measured on a Bruker AVANCE-400 at 400 MHz for ^{1}H-NMR, 100 MHz for ^{13}C-NMR, and 125 MHz for ^{31}P-NMR, respectively, in CDCl$_3$. The chemical shifts (δ) are reported in ppm downfield from TMS as an internal standard or from the residual solvent peak for ^{1}H- and ^{13}C-NMR. Coupling constants (J) are reported in Hz. Low

resolution mass spectra (MS) were recorded by the JEOL JMS-K9 spectrometers. Elemental analysis was recorded on a Perkin-Elmer 2400CHN elemental analyzer. Column chromatography was performed on silica gel (E. Merck). Absorption and fluorescence spectra were recorded on a U-3310 spectrometer (Hitachi) and on a RF-5000 spectrometer (Shimadzu), respectively. Fluorescence quantum yields (Φ_F) were estimated using 9,10-diphenylanthracene ($\Phi_F = 0.91$ in benzene) as a standard. The measurements of the total chemiluminescence quantum yield (Φ_{CL}) were carried out by a photon-counting method using a Hamamatsu Photonics R464 photomultiplier connected to a photon-counting unit (C3866) and a photon-counting board M8784 according to a previously reported procedure [16], and the luminol chemiluminescence was used as the standard in DMSO for calibration of the photomultiplier tube.

Materials

All commercially available chemicals and solvents were of the highest purity or purified by the standard method. The known compound, 4,4'-bis[(2'-ethylhexyloxy)styryl]stilbene (**3**), was prepared according to the reported procedure by us (20).

Synthesis of 4-(2'-ethylhexyloxy)benzylphosphonic acid diethyl ester

A mixture of triethyl phosphite (6 mL, 34.4 mmol) and 4-(2'-ethylhexyloxy)benzyl bromide (10.2 g, 34.3 mmol), prepared from *p*-hydroxybenzaldehyde by alkylation with 2-ethylhexyl bromide, reduction to the alcohol, and bromination with hydrobromic acid, was heated at 130 °C overnight. Purification by column chromatography gave the product as a colorless oil (10. 5 g, 86%). ^{1}H-NMR δ 0.88-0.94 (m, 6H, OCH$_2$CH(CH$_2$C*H*$_3$)(CH$_2$)$_3$C*H*$_3$), 1.24   (t, 6H, J = 7.07 Hz, P(O)(OCH$_2$C*H*$_3$)$_2$), 1.27-1.53 (m, 8H, OCH$_2$CH(C*H*$_2$CH$_3$)(C*H*$_2$)$_3$CH$_3$), 1.71 (septet, 1H, J = 6.03 Hz, OCH$_2$C*H*(CH$_2$CH$_3$)(CH$_2$)$_3$CH$_3$), 3.82 (d, 2H, J = 6.03, Hz, OC*H*$_2$C$_7$H$_{15}$), 3.96-4.05 (m, 4H, OCH$_2$P(O)(OC*H*$_2$CH$_3$)$_2$), 3.08 (d, 2H, J_{HP} = 21.0 Hz, OC*H*$_2$P(O)), 6.84(d, 2H, J = 8.04 Hz, Ar-*H*), 7.19 (dd, 2H, J = 2.53, 8.59 Hz, Ar-*H*). ^{31}P NMR (85% phosphoric acid as an external standard), δ 27.3.

Synthesis of 4'-(2"-ethylhexyloxy)-4-(2'-ethylhexyloxy)stilbene (1)

To a suspension of *tert*-BuOK (1.43 g, 12.8 mmol) in THF (tetrahydrofuran) (15 mL) was added a solution of the phosphonic acid ester (2.28 g, 6.40 mmol) prepared above in THF (20 mL) and a solution of 4-(2'-ethylhexyloxy)benzaldehyde (1 g, 4.27 mmol) in THF (20 mL) in this order under

a nitrogen atmosphere. After the solution was stirred for 4 h at an ambient temperature, the solvent was removed under a reduced pressure and the residue was treated with benzene and saturated ammonium chloride solution. The organic layer was washed with brine and dried over anhydrous sodium sulfate. Removal of the solvent and purification by column chromatography on a silica gel using benzene as an eluant gave the product as a white powder (1.25 g, 76 %). M.p 74-78 $^{\circ}$C. ^{1}H-NMR, δ 0.88-0.95 (m, 12 H, OCH$_2$CH(CH$_2$CH_3)(CH$_2$)$_3$CH_3), 1.30-1.49 (m, 16H, OCH$_2$CH(CH_2CH$_3$)(CH_2)$_3$CH$_3$), 3.85 (d, 4H, J = 5.6 Hz, OCH_2), 6.88 (d, 4H, J = 8.4 Hz, Ar-H), 6.91 (s, 2H, CH=CH), 7.40 (d, 2H, J = 8.4 Hz, Ar-H). MS m/z = 436 (M^{+}). Anal. Calcd for C$_{30}$H$_{44}$O$_2$, C, 82.52; H, 10.16 (%). Found, C; 82.67, H; 10.18 (%).

Synthesis of 1,4-bis[(2'-ethylhexyloxy)styryl]benzene (2)

To a suspension of *tert*-BuOK (1.16 g, 7.16 mmol) in DMF (dimethyl formamide) (10 mL) was added a solution of the phosphonic acid ester (2.55 g, 7.16 mmol) in DMF (10 mL) and under a solution of terephthalaldehyde (0.48 g, 3.58 mmol) in DMF (19 mL) in this order under a nitrogen atmosphere. After the solution was stirred overnight at an ambient temperature, the solvent was removed and the residue was treated with ethyl acetate, diluted hydrochloric acid, and saturated ammonium chloride solution. The organic layer was washed with brine and dried over anhydrous sodium sulfate. Removal of the solvent and purification by column chromatography on a silica gel using benzene as an eluant gave the product as a yellow crystal (0.77 g, 40 %). M. p. 187-190 $^{\circ}$C. ^{1}H-NMR δ 0.89-0.95 (m, 12H, OCH$_2$CH(CH$_2$CH_3)(CH$_2$)$_3$CH_3), 1.30-1.55(m, 16H, OCH$_2$CH(CH_2CH$_3$)(CH_2)$_3$CH$_3$), 1.73 (septet, 2H, J = 6.06 Hz, OCH$_2$CH(CH$_2$CH$_3$)(CH$_2$)$_3$CH$_3$), 3.86 (dd, 4H, J = 0.76, 6.06 Hz, OCH_2C$_7$H$_{15}$), 6.89 (d, 4H, J = 8.59 Hz, Ar-$\underline{H}$), 6.96(d, 2H, J = 16.2 Hz, CH=CH), 7.07(d, 2H, J = 16.2 Hz, CH=CH), 7.44 (d, 4H, J = 8.59 Hz, Ar-H), 7.46 (s, 4H, Ar-H). ^{13}C-NMR, δ 11.50, 14.47, 23.44, 24.27, 29.49, 30.93, 39.79, 71.01, 115.16, 126.47, 126.90, 128.03, 130.33, 137.06, 159.57. Anal. Calcd for C$_{38}$H$_{50}$O$_2$, C, 84.71; H, 9.35 (%). Found, C, 84.53; H, 9.35 (%).

Synthesis of 1,3-bis[(2'-ethylhexyloxy)styryl]benzene (4)

This compound was prepared according to the procedure similar to the above olefination reaction using *tert*-BuOK (1.08 g, 9.42 mmol), the phosphonic acid ester (2.01 g, 5.64 mmol), and isophthalaldehyde (0.48 g, 3.58 mmol) in THF. The product was obtained in 53 % yield (0.81 g) as a white solid. M. p. 69-71 $^{\circ}$C. ^{1}H-NMR, δ 0.89-0.95 (m, 12H, OCH$_2$CH(CH$_2$CH_3)(CH$_2$)$_3$CH_3), 1.30-1.53 (m, 16H, OCH$_2$CH(OCH_2CH$_3$)(CH_2)$_3$CH$_3$), 1.73 (septet, 2H, J = 6.06 Hz,

OCH$_2$C*H*(CH$_2$CH$_3$)(CH$_2$)$_3$CH$_3$), 3.86 (d, 4H, *J* = 5.81 Hz, OC*H*$_2$C$_7$H$_{15}$), 6.90 (d, 4H, *J* = 8.59 Hz, Ar-*H*), 6.98 (d, 2H, *J* = 16.4 Hz, CH=C*H*), 7.10 (d, 2H, *J* = 16.2 Hz, C*H*=CH), 7.29-7.37 (m, 3H, Ar-*H*), 7.45 (d, 4H, *J* = 8.84 Hz, Ar-*H*), 7.59 (s, 1H, Ar-*H*). ^{13}C NMR, δ 11.51, 14.48, 23.45, 24.28, 29.50, 30.94, 39.80, 71.01, 115.17, 124.61, 125.44, 126.72, 128.09, 128.93, 129.28, 130.25, 138.44, 159.63. Anal. Calcd for C$_{38}$H$_{50}$O$_2$, C, 84.71; H, 9.35 (%). Found. C, 84.60; H, 9.35 (%).

Synthesis of 1,2-bis[(2'-ethylhexyloxy)styryl]benzene (5)

This compound was prepared according to the procedure similar to the olefination reaction described above using *tert*-BuOK (0.23 g, 2.08 mmol), the phosphonic acid ester (0.74 g, 2.09 mmol), and phthalaldehyde (1.04 g, 1.04 mmol) in DMF. The product was obtained in 17 % yield (0.096 g) as a yellow liquid. ^{1}H NMR, δ 0.86-0.95 (m, 12H, OCH$_2$CH(CH$_2$C*H*$_3$)(CH$_2$)$_3$C*H*$_3$), 1.23-1.55 (m, 16H, OCH$_2$CH(C*H*$_2$CH$_3$)(C*H*$_2$)$_3$CH$_3$), 1.74 (septet, 2H, *J* = 6.03 Hz, OCH$_2$C*H*(CH$_2$CH$_3$)(CH$_2$)$_3$CH$_3$), 3.87 (dd, 4H, *J*=1.01, 6.03 Hz, OC*H*$_2$C$_7$H$_{15}$), 6.90 (d, 4H, *J* = 8.84 Hz, Ar-*H*), 6.94 (d, 2H, *J* = 16.2 Hz, CH=C*H*), 7.32 (d, 2H, *J* = 16.2 Hz, C*H*=CH), 7.36 (s, 2H, Ar-*H*), 7.45 (d, 4H, *J*=8.84 Hz, Ar-*H*), 7.54-7.57(m, 2H, Ar-*H*).

Synthesis of 1,3,5-tris(dimethylphosphonomethyl)benzene

A mixture of trimethyl phosphite (6.2 mL, 52.6 mmol) and 1,3,5-tri(bromomethyl)benzene (6.13.g, 17.2 mmol), prepared from trimesic acid (1,3,5-benzenetricarboxylic acid) by esterfication with ethanol followed by reduction with LiALH$_4$ and then bromination with hydrobromic acid, was heated overnight at 120 ^{o}C. Removal of the by-products such as ethyl bromide and dimethyl methylphosphonate under a reduced pressure and treatment with petroleum ether gave a white solid (6.43 g, 84 %). ^{1}H-NMR, δ 3.14 (d, 6H, *J*$_{HP}$ = 22.2 Hz, C*H*$_2$), 3.68 (d, 18H, OC*H*$_3$), 7.14 (s, 3H Ar-*H*). ^{31}P-NMR (85 %, phosphoric acid as an external standard), δ 29.1.

Synthesis of 1,3,5-tris[(2'-ethylhexyloxy)styryl]benzene (6)

This compound was prepared according to the procedure similar to the olefination reaction described above using *tert*-BuOK (0.68 g, 6.08 mmol), 1,3,5-tris(dimethylphosphono-methyl)benzene (1.01 g, 2.28 mmol), and 4-(2'-ethylhexyloxy)benzaldehyde (1.02 g, 4.34 mmol) in DMF. The product was obtained as a yellow liquid (0.30 g, 17 %). ^{1}H-NMR, δ 0.89-0.96 (m, 18H, OCH$_2$CH(CH$_2$C*H*$_3$)(CH$_2$)$_3$C*H*$_3$), 1.23-1.56 (m, 24H, OCH$_2$CH(C*H*$_2$CH$_3$)(C*H*$_2$)$_3$CH$_3$), 1.74 (septet, 3H, *J* = 6.06 Hz, OCH$_2$C*H*(CH$_2$CH$_3$)(CH$_2$)$_3$CH$_3$), 3.87 (dd, 6H, *J* = 1.01, 6.06 Hz, OC*H*$_2$C$_7$H$_{15}$),

6.91 (d, 6H, J = 8.59 Hz, Ar-H), 7.00 (d, 3H, J = 16.2 Hz, CH=CH), 7.14 (d, 3H, J = 16.2 Hz, CH=CH), 7.47 (d, 6H, J = 8.59 Hz, Ar-H), 7.48 (s, 3H, Ar-H). ^{13}C NMR, δ 11.54, 14.48, 23.46, 24.28, 29.50, 30.94, 39.80, 71.02, 115.18, 123.48, 126.66, 128.12, 129.10, 130.25, 138.71, 159.66.

Measurement of Φ_{CL}

For a typical run, a solution containing the oxalates in THF (0.5 mL, 7.5 x 10^{-4} M) was added to a solution (1,5 mL) containing sodium carbonate (2.5 x 10^{-4} M), fluorophores (1.0 x 10^{-4} M), hydrogen peroxide (4.0 x 10^{-2} M), and the surfactants of various concentrations in distilled water in a quartz cell placed in front of the photomultiplier at 25 ^{o}C. The photons generated over a 1000 sec. period were counted. The average of the values obtained by a few measurements was used for the calculation of Φ_{CL}.

Results and Discussion

Absorption and fluorescence spectra of the oligophenylenevinylene fluorophores

The structures of the oligophenylenevinylenes used in this study are shown in Fig. 1. 2-Ethylhexyloxy (OEH) groups were introduced as the residues enhancing both the electron-donating properties and the solubility toward organic solvents (21,22). Their selected physical properties are shown in Table 1, in which some pronounced characteristics should be noted. Comparing the three oligophenylenevinylenes (1–3) with linearly extended conjugate systems, the extension of the conjugated system leads to a red-shift in the maximum absorption and fluorescence wavelengths and an increase in the fluorescence quantum yields (ΦF). In addition, it is interesting to note that the oxidation potential (Eox) deeply involved with the CL efficiency tends to become higher with extension of the π-conjugation. The highest Stokes shift was found in 5, which suggests the specific character of this compound with the ortho-occupation of two styryl groups, namely, steric hindrance would provide significantly different structures between the ground and excited states. Fluorophore 6, with a dendritic structure, is characterized by shorter absorption and emission wavelengths compared with the others (23).

PO-CL using the oligophenylenevinylenes as fluorophores

The CL reactions of TCPO in the presence of fluorophores 1–6 were carried out under basic conditions in aqueous THF, in which conditions including the solvents and reagents were

chosen to achieve better results. For example, aqueous THF was used as the solvent for this system, instead of aqueous acetonitrile frequently used for PO-CL reactions because of the

solubility of the reactants, TCPO and fluorophores, and either potassium or sodium carbonates was used for better CL efficiency. The results are summarized in Table 2. Because the CL and fluorescence spectra for the used fluorophores were in good agreement, light emission was produced in an indirect manner to form excited fluorophores by energy transfer from the high-energy intermediates to the fluorophores.

The singlet excitation yield (ΦS)was calculated fromthe equation, $\Phi CL = \Phi r Å \sim \Phi S Å \sim \Phi F$, where ΦCL, Φr and ΦF are the total CL quantum yield, the yield of the chemical reaction, regarded as unity for the complete consumption of TCPO during the reactions, and the fluorescence quantum yield.Whereas the highest ΦCL was recorded using 2 as a fluorophore, ΦS was the greatest when 1 was used, which can be explained by a chemically initiated electron-exchange luminescence process (24–26) because of the close relation between the oxidation potentials of 1, 2 and 3 and that of ΦS. Despite the smaller ΦCL values of the three distyrylbenzenes 4, 5 and 6, compared with that of 2, the dendritic fluorophore 6 is also a good fluorophore for this CL system. This is probably due to the electron-donating ability of 6 by three alkoxy groups attached to the ends of the dendritic molecule.

Next, two aryl oxalates, 7 and 8, bearing ester groups with long alkyl chains, i.e. lauryl groups, at the meta- and para-positions, respectively, were prepared to explore the interaction between the oxalates and various kinds of surfactants (vide infra). The CL reaction was carried out in aqueous THF in the presence of 2 as a fluorophore under basic conditions. The results are shown in Table 3, in which the values of ΦCL reflect T3 the reactivity of the oxalates. The CL efficiency was related to the acidity of the phenoxy groups as the leaving groups (17). Thus, 7 was more reactive than 8, and TCPO is 20–50 times more reactive than the others.

Effect of surfactants on the chemiluminescence efficiency

To study their effect on CL efficiency, four categories of surfactants, anionic, cationic, amphoteric and non-ionic (Table 4), were employed in PO-CL enhanced by the distyrylbenzene

fluorophore 2. Changes in the ΦCL of the PO-CL were measured using three oxalates, TCPO, 7 and 8 at each surfactant concentration, in which the concentrations of the surfactants were well above their CMCs. The results are shown in Fig. 2.

When the anionic surfactant SDS was added, a remarkable increase in ΦCL was observed with increasing SDS concentration, whereas in the case of SDBS, a constant ΦCL value was maintained after its increase at a lower concentration of this surfactant. A similar tendency of SDS to increase the ΦCL in the PO-CL using other fluorophores, 4, 5 and 6, shows that the positive effect of SDS is

common in the PO-CL system. The effect of anionic surfactants was furthermore established by enhancement of the CL efficiency when SHDS and STDS with longer alkyl chains than SDS were used, as shown in Fig. 3. By contrast, the opposite results F3 were observed when cationic surfactants were employed. A sharp decrease in ΦCL was detected with increasing concentrations of the cationic surfactants DTAB and DPC. Interestingly, the amphoteric surfactant, SB-12, having a cationic site within the chain and an anionic site at the end, behaved like both cationic and anionic surfactants, in which ΦCL decreased after an initial increase. The non-ionic surfactant, Briji 35, produced different results among the three oxalates, namely, ΦCL initially increased, but decreased with increasing surfactant concentration for the reaction of TCPO, whereas a sharp increase was found in the case of oxalates 7 and 8 with the long alkyl chains. In addition, the non-ionic surfactants, Brij 58 and Brij 78, with alkyl chains longer than Brij 35, were also used in the PO-CL reactions of oxalates 7 and 8. Whereas Brij 58 was effective on ΦCL enhancement, similarly to Brij 35, Brij 78 with the longest alkyl chain was unexpectedly inferior to the others at the higher concentration.

These results indicate some important concerns about the effect of surfactant on PO-CL reactions. CL reactions proceed within a micellar system, but not within an inverted micellar system in mixed THF and water solvents (THF : H2O = 3 : 1), because of the different results for SDS and SDBS. A similar tendency should have been observed if the reactions occur in reaction fields surrounded by the anionic moieties of the inverted micelles formed by either SDS or SDBS. The difference in the behavior of SDS and SDBS is based on their structures, the latter of which is distinguished from SDS by the presence of a benzene ring at the end of the surfactant. In the present CL reaction, the hydrophobic chemical species are taken into the SDBS micelle core less effectively than in the SDS micelle core, because the dodecyl chains in SDBS micelles are more tightly packed and less flexible than those in SDS micelle (27,28). Since the fluorescence spectra of 2 did not change at the various SDS concentrations, an increase in ΦCL with the increase in ΦF of 2 in the hydrophobic spheres of the micelles is ruled out. The remarkable effect of the anionic surfactants, SDS, STDS and SHDS, can be explained by the increasing concentration of the interacting chemical species concerning the chemiexcitation process in the hydrophobic region of the SDS micelle, although the longer alkyl chain of these surfactants did not exactly give the higher CL efficiency. Here, it is important to note that the high-energy intermediates, the 4-aryloxy-4-hydroxy-1, 2-dioxetane-3-ones (17) or 1,2-dioxetane-3,4-dione, are formed by the reaction of oxalates with alkaline hydrogen peroxide and will concentrate and interact with the fluorophorewithin the hydrophobic area in the micelle. The higher the concentration of the anionic surfactants, the more the micelle number increases. It might be more important that these anionic surfactants prevent a rapid degradation of the oxalates by the hydrolysis under alkaline conditions

(8,29,30), because the negatively charged sulfate moiety of SDS would interrupt the contact between the active oxalates and the hydroxyl anions at the hydrophobic inside of the SDS micelle by the repulsive force of the negatively charged sulfate moieties at the periphery of themicelle. By contrast, the cationic surfactants take the hydroxyl ions in the micelle core to promote a significant degradation of the oxalates. The negative effect of DTAB is not completely due to the fluorescence quenching effect of a bromide ion, as sometimes mentioned, but chiefly due to its cationic character, because DPC as well as SB-12 showed a negative effect. However, the effect of SDS cannot explain the difference in CL efficiency among the oxalates, TCPO, 7 and 8, as shown in Fig. 2, namely, TCPO and 8 showed CL efficiencies five times larger than 7, and therefore the reactivity of the oxalates did not correlate completely with their CL efficiencies in this system. Finally, despite some points not being well elucidated, the surfactant effect is highly dependent on the surfactant properties, that is, various effects would occur based on the choice of the luminophore, fluorophore and surfactant.

Conclusions

Some fluorescent oligophenylenevinylenes were used in PO-CL as fluorophores, and the distyrylbenzenes were found to be the most effective enhancer of all in this study. The effect of surfactants on CL efficiency was also investigated in a PO-CL system enhanced by the distyrylbenzene fluorophore. The anionic surfactant showed a positive effect, increasing efficiency of the three oxalate CL reactions, whereas cationic surfactants led to reduced CL efficiency as their concentrations increased. The affinity of the alkyl chains introduced into the oxalates for the non-ionic surfactants contributed to the increase in CL intensities. Protection of the active oxalates from rapid alkaline hydrolysis by the surfactants is important, as is the concentration of the reactants at the hydrophobic micelle core.

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Captions

Fig. 1   Structures of oligophenylenevinylene fluorophores used in the present study.

Fig. 2. Effect of the surfactants on the CL efficiencies using three oxalates, TCPO, **7**, and **8**. THF: H_2O = 3:1, [oxalates] = 1.88 x 10^{-4}M, [Na_2CO_3] = 1.88 x 10^{-4}M, [**2**] = 0.75 x 10^{-4}M, [H_2O_2] = 3.0 x 10^{-2}M.

Fig. 3. Effect of anionic surfactants on the TCPO PO-CL. THF: H_2O = 3:1, [TCPO] = 1.88 x 10^{-4}M, [Na_2CO_3] = 1.88 x 10^{-4}M, [**2**] = 0.75 x 10^{-4}M, [H_2O_2] = 3.0 x 10^{-2}M.

Table 1.   Physical properties of fluorophores **1-6**.

Foot notes:

[a] Measured in THF at 1.0 x 10^{-5} M.
[b] The data in the prentheses are the values measured in THF and water in the ratio of 3:1.
[c] Measured in CH_2Cl_2. [fluorophores] = 1.0 x 10^{-4} M, [Bu_4NClO_4] = 0.1 M.
[d] Not measured.

Table 2. Chemiluminescence quantum yields of peroxyoxalate chemiluminescence using TCPO in the presence of the fluorophores **1-6**.

Foot notes:

[a] THF : H_2O = 3:1, [TCPO] = 1.0 x 10^{-5} M, [fluorophore] = 1.0 x 10^{-5} M, [H_2O_2] = 1.0 x 10^{-2} M, [K_2CO_3] = 2.0 x10^{-4} M.
[b] THF : H_2O = 3:1, [TCPO] = 2.5 x 10^{-6} M, [fluorophore] = 2.5 x 10^{-6} M, [H_2O_2] = 2.5 x 10^{-3} M, [K_2CO_3] = 5.0 x10^{-5} M.
[c] [TCPO] = 5.0 x 10^{-5} M, [fluorophore] = 1.0 x 10^{-4} M, [Na_2CO_3] = 7.5 x 10^{-4} M, [H_2O_2]= 1.2 x 10^{-1}M.
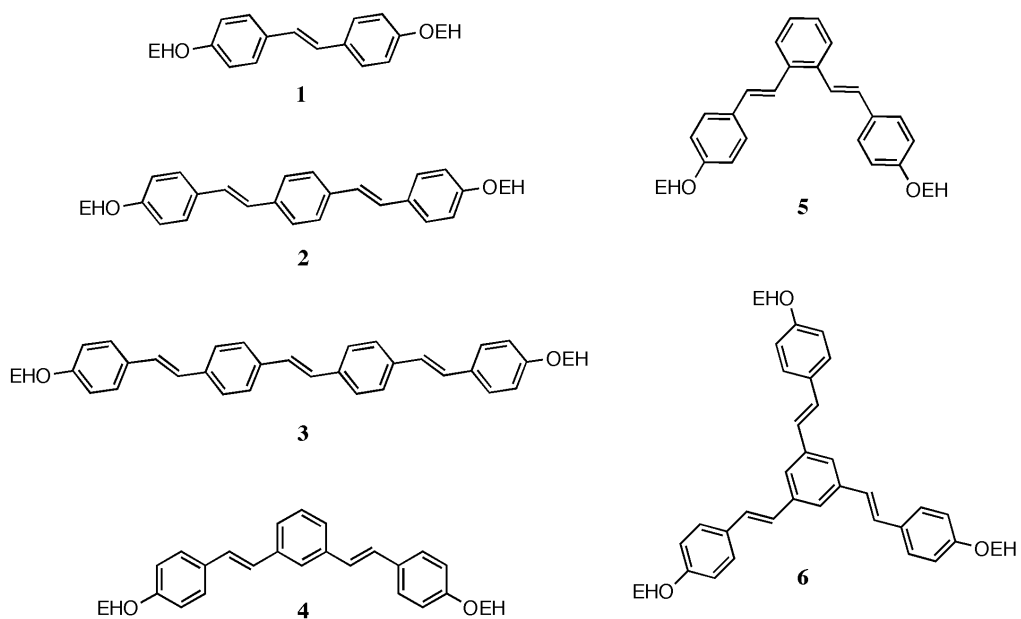
Table 3. Chemiluminescence quantum yield of oxalates, **TCPO**, **7** and **8** in the presence of **2** as a fluorophore.

Foot notes:

[a] A mixture of THF and water (3;1) was used as the solvents. [oxalate] = 5.0 x 10^{-5} M, [**2**] = 1.0 x 10^{-4} M, [Na_2CO_3] = 7.5 x 10^{-4} M,
   [H_2O_2] = 1.2 x 10^{-2} M.

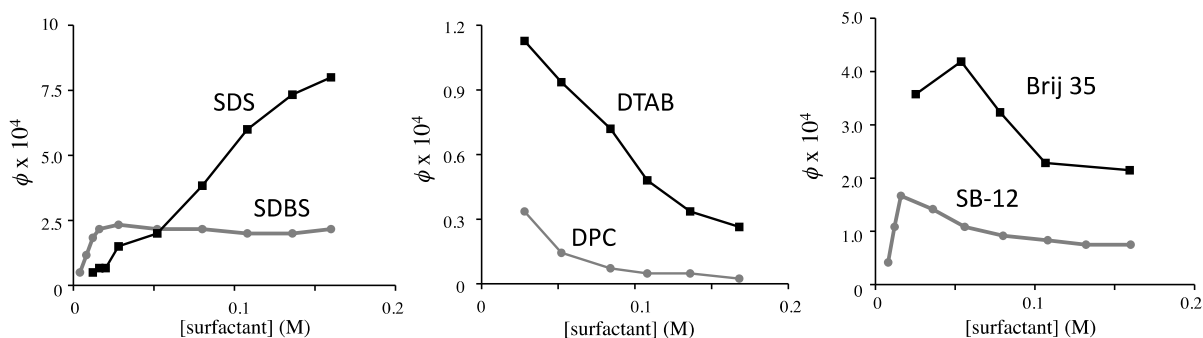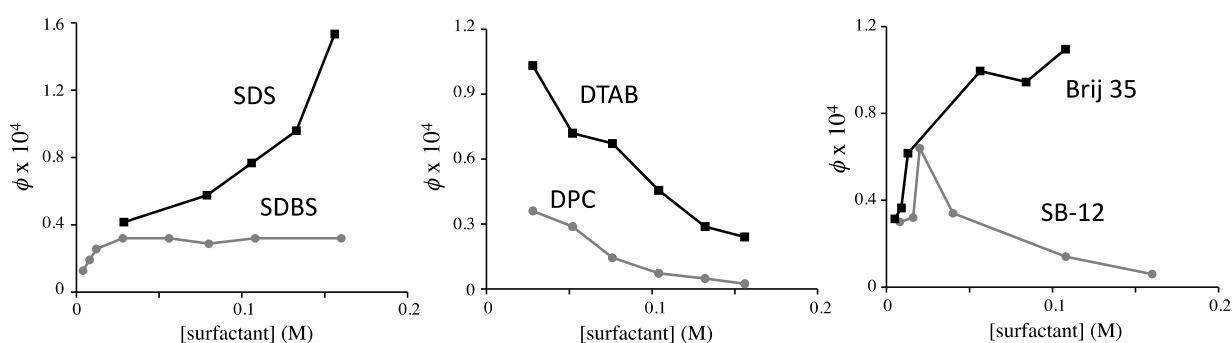**Table 4.** Structure of surfactants used in the present study.

Figures 1-3

Fig. 1. Structures of the fluorophores **1-6**.

TCPO-POCL enhanced by **2** in the presence of surfactants

Oxalate **7**-POCL enhanced by **2** in the presence of surfactants

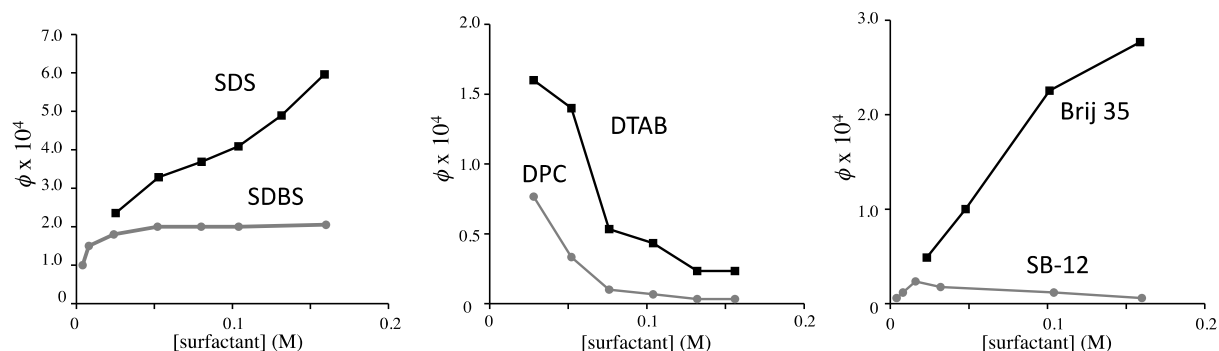## Oxalate **8**-POCL enhanced by **2** in the presence of surfactants

Fig. 2. Effect of the surfactants on the CL efficiencies using three oxalates, TCPO, **7**, and **8**.
THF: H_2O = 3:1, [oxalates] = 1.88 x 10^{-4}M, [Na_2CO_3] = 1.88 x 10^{-4}M, [**2**] = 0.75 x 10^{-4}M,
[H_2O_2] = 3.0 x 10^{-2}M.
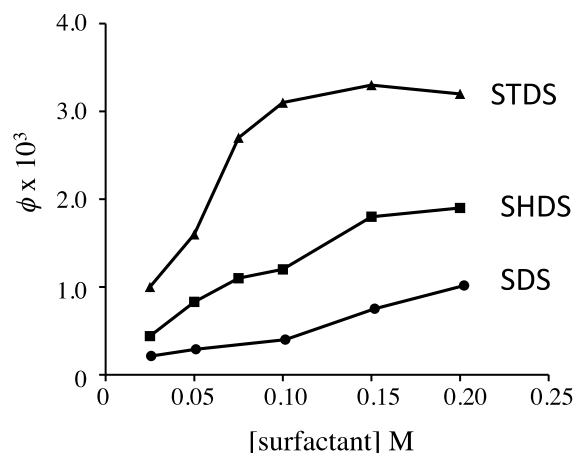
Fig. 3. Effect of anionic surfactants on the TCPO PO-CL.
THF: H_2O = 3:1, [TCPO] = 1.88 x 10^{-4}M,
[Na_2CO_3] = 1.88 x 10^{-4}M, [**2**] = 0.75 x 10^{-4}M,
[H_2O_2] = 3.0 x 10^{-2}M.

Tables 1-4

Table 1. Physical properties of fluorophores **1-6**.

	Abs. ⏐ max.[a, b] nm	EM. ⏐ max.[a] nm	F_F [a,b]	$E_{1/2OX}$ [c] V vs, SCE
1	348	382	0.23	0.89
2	368 (368)	432	0.71(0.67)	1.03
3	388	436	0.93	1.26
4	(325)	431	(0.20)	--- [d]
5	(296)	428	(0.15)	--- [d]
6	328 (328)	398	0.35 (0.32)	--- [d]

[a] Measured in THF at 1.0 x 10^{-5} M. Estimated by comparison with 9,10-diphenylanthracene as a standard ($\sqrt{}_F$ = 0.95). [b] The data in the prentheses are the values measured in THF and water in the ratio of 3:1. [c] Measured in CH_2Cl_2. [fluorophores] = 1.0 x 10^{-4} M, [Bu_4NClO_4] = 0.1 M. [d] Not measured.

Table 2. Chemiluminescence quantum yields of peroxyoxalate chemiluminescence using TCPO in the presence of the fluorophores **1-6**.
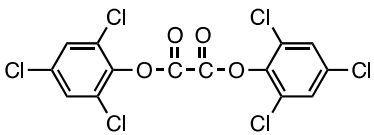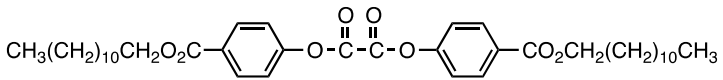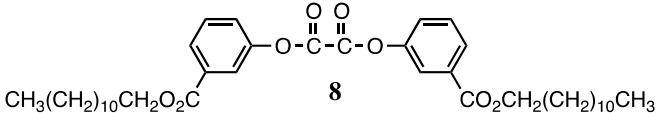
	$F_{CL} \times 10^4$ einstein/ mol	$F_S \times 10^4$ einstein/ mol
1	2.2 ^{a}	9.6
2	3.9 ^{b}	4.2
3	1.2 ^{c}	1.3
4	0.22 ^{c}	2.7
5	0.13 ^{c}	2.1
6	0.67 ^{c}	5.0

^{a} THF : H_2O = 3:1, [TCPO] = 1.0 x 10^{-5} M, [fluorophore] = 1.0 x 10^{-5} M, [H_2O_2] = 1.0 x 10^{-2} M, [K_2CO_3] = 2.0 x10^{-4} M.
^{b} THF : H_2O = 3:1, [TCPO] = 2.5 x 10^{-6} M, [fluorophore] = 2.5 x 10^{-6} M, [H_2O_2] = 2.5 x 10^{-3} M, [K_2CO_3] = 5.0 x10^{-5} M.
^{c} [TCPO] = 5.0 x 10^{-5} M, [fluorophore] = 1.0 x 10^{-4} M, [Na_2CO_3] = 7.5 x 10^{-4} M, [H_2O_2]= 1.2 x 10^{-1}M.
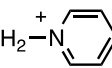
Table 3. Chemiluminescence quantum yield of oxalates, **TCPO**, **7** and **8** in the presence of **2** as a fluorophore.

oxalate	Φ_{CL} einstein/mol	rel.Φ_{CL}
TCPO	1.4 x 10^{-4}	1.0
7	7.5 x 10^{-6}	0.05
8	1.3 x 10^{-6}	0.02

^{a} A mixture of THF and water (3;1) was used as the solvents. [oxalate] = 5.0 x 10^{-5} M, [**2**] = 1.0 x 10^{-4} M, [Na_2CO_3] = 7.5 x 10^{-4} M, [H_2O_2] = 1.2 x 10^{-2} M.

Table 4. Structure of surfactants used in the present study.

anionic surfactant	$CH_3(CH_2)_{10}CH_2OSO_3^- Na^+$ SDS	$CH_3(CH_2)_{12}CH_2OSO_3^- Na^+$ STDS
	$CH_3(CH_2)_{14}CH_2OSO_3^- Na^+$ SHDS	$CH_3(CH_2)_{10}CH_2$—⟨benzene⟩—$SO_3^- Na^+$ SDBS

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cationic surfactant	$CH_3(CH_2)_{10}CH_2\overset{+}{N}(CH_3)_3\ Br^-$ DTAB	$CH_3(CH_2)_{10}CH_2-\overset{+}{N}⟨pyridine⟩\ Cl^-$ DPC

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amphoteric surfactant	$CH_3(CH_2)_{10}CH_2\overset{+}{N}(CH_3)_2CH_2CH_2OSO_3^-$ SB-12

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non-ionic surfactant	$C_{12}H_{25}(OCH_2CH_2)_{23}OH$ Brij 35	$C_{16}H_{33}(OCH_2CH_2)_{20}OH$ Brij 58	$C_{18}H_{37}(OCH_2CH_2)_{23}OH$ Brij 78