

The Hammett correlation between distyrylbenzene substituents and chemiluminescence efficiency providing various ρ -values for peroxyoxalate chemiluminescence of several oxalates

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Key Words:

Peroxyoxalate chemiluminescence

Hammett correlation

High-energy intermediate

Frontier molecular orbital theory

ABSTRACT

Peroxyoxalate chemiluminescence (PO-CL) was investigated using eight oxalates with various phenol moieties and the distyrylbenzene (DSB) fluorophores with various substituents. The ρ -values in the Hammett correlation between the substituent constants (σ_p^+) of the DSBs and the singlet chemiexcitation yields (Φ_S) for the PO-CL reactions varied from -0.50 to -1.01 depending on the oxalate structure, and the reactive oxalates tended to afford the higher absolute ρ -values but with a few exceptions. Based on the CIEEL mechanism, these experimental observations suggest that the aryloxy groups still remain in the 1,2-dioxetanones (DOTs), which are the postulated high-energy intermediates, and control the electronic properties of DOTs as electron-acceptors. The LUMO energies of the DOTs calculated by the *ab initio* method with a B3LYP/6-31g(d) basis set reveal that the lower the DOT-LUMO energies, the higher the absolute ρ -values were provided for the corresponding oxalates, as predicted by the frontier molecular orbital (FMO) theory. Thus, the chemical species interacting with the DSBs would be not unitary and will be DOTs.

1. Introduction

Since Chandross first discovered the peroxyoxalate chemiluminescence (PO-CL) reaction [1], much attention has been paid to this CL and chemists have tried to elucidate its mechanism for a long time [2-25] because of high efficiency [23] and usefulness in analytical chemistry [26,27]. Among the several peroxides proposed so far as the high-energy intermediates (HEIs) capable of generating the excited fluorophores during their decomposition, the four-membered cyclic peroxides, such as 4-aryloxy-4-hydroxy-1,2-dioxetane-3-one (DOT) and 1,2-dioxetane-3,4-dione (DOD), have been the most frequently proposed [3,4,6,7,9,10,14,19,21,22]. However, these intermediates have never been captured nor isolated. There have been studies observing labile intermediates by NMR using the highly reactive oxalates [28,29]. In addition, the EPR detection of a biradical as a trace of the formed DOD during the reaction of the oxalyl chloride and hydrogen peroxide spectra was very recently reported [30]. CIEEL (chemically initiated electron exchange luminescence) mechanism [31,32] was applied to the PO-CL [33,34], and explained experimental evidences [35-40]. According to this mechanism, an electron transfer from the fluorophores to the HEI, such as the DOTs or DOD, takes place to form a pair consisting of the carbon dioxide radical anion and the fluorophore radical cation during the decomposition of the HEI, which is followed by a back electron transfer to produce the excited fluorophores (Scheme 1). In spite of a steady accumulation of knowledge and many recent efforts made by a number of chemists, identification of the HEIs interacting with fluorophores still remains unclear.

It is important to examine the effect of the oxalate structures on the CL behavior [22], because there have been only a few reports in which a number of oxalates were employed, and new aspects can be obtained by comparing the CL behavior of the different oxalates, if the structure of the HEI as the electron-acceptors is not unitary and might depend on the oxalate structures. On the other hand, the 1,4-distyrylbenzene (DSB) derivatives are strongly fluorescent [41,42] and good emitters among the numerous fluorophores so far used for the PO-CL reactions [38,39] due to availability by the simple synthetic method and capability of modulating their electronic properties by the substituents. During our continuous studies of the DSB enhanced PO-CL, some remarkable electronic effects on the CL efficiency have been observed. Therefore, it is expected that there is a possibility of identification of the HEIs when the CL behavior using various DSBs and oxalates is investigated in detail. In this paper, we report the Hammett correlation between the DSB substituents and the behavior of the DSB enhanced PO-CL reactions employing the eight aryl oxalates and give consideration to the HEIs in connection with the interpretation of the observed CL behavior using the frontier molecular orbital (FMO) theory.

2. Experimental details

2.1. Materials

Melting points were determined using a hot stage microscope apparatus and were uncorrected. Proton nuclear magnetic resonance ^1H - and ^{13}C -NMR spectra were measured on a Bruker AVANCE-400 at 400 MHz for ^1H -NMR, 100 MHz for ^{13}C -NMR, respectively, in CDCl_3 . The chemical shifts (δ) are reported in ppm downfield from TMS as internal standard or from the residual solvent peak for ^1H - and ^{13}C -NMR. Coupling constants (J) are reported in Hz. Low and high resolution mass spectra (MS) were recorded by the JEOL JMS-K9 spectrometers. Elemental analysis was recorded on a Perkin-Elmer 2400CHN elemental analyzer. Analytical TLC was carried out on precoated silica gel 60F-254 plates (E. Merck). 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. The measurements of the total CL 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, and the luminol CL [$\Phi_{\text{CL}} = 0.09$ in dimethyl sulfoxide, Lit. J. Lee, H. H. Seliger, Photochem. Photobiol. 15 (1972) 227-237] was used as the standard in DMSO for calibration of the photomultiplier tube.

All commercially available chemicals and solvents were of the highest purity or purified by the standard method. A series of the oxalates employed in the present study, all of which are known compounds, are listed in Table 1. They were prepared from the reaction of oxalyl chloride and two equivalents of the corresponding phenols in the presence of triethylamine in benzene, while the unsymmetrical oxalate 4-CPPO was prepared from the reaction of oxalyl chloride and one equivalent phenol in the presence of triethylamine followed by the addition of another *p*-chlorophenol. DNPO [bis(2,4-dinitrophenyl) oxalate] was supplied by Tokyo Chemical Industries (TCI).

2.1.1. 1,4-Bis(2-ethylhexyloxy)-2,5-bis(diethylphosphonomethyl)benzene

2-Ethylhexyl bromide (35 g, 180 mmol) was added dropwise to a solution of hydroquinone (10 g, 91 mmol) and potassium hydroxide (13 g, 230 mmol) in ethanol (80 mL) and stirred for 2 h at 80°C. After removal of the solvent and the addition of ether, the inorganic by-products were removed by washing with saturated NaHCO_3 aqueous solution and brine. The organic phase was dried over anhydrous Na_2SO_4 . After the Na_2SO_4 was filtered out and the solvent was distilled away, the crude product was purified by column chromatography on silica gel (eluant: *n*-hexane) to afford

1,4-bis(2-ethylhexyloxy)benzene as a colorless liquid. Yield: 50% (15 g); ^1H NMR (400 MHz, CDCl_3) δ 0.87-0.94 (m, 12H, $-\text{CH}_3$), 1.29-1.53 (m, 16H, $-\text{CH}_2-$), 1.66-1.72 (m, 2H, $>\text{CH}-$), 3.78 (d, 4H, $-\text{CH}_2\text{O}-$, $J = 5.8$ Hz), 6.82 (s, 4H, Ar-H). After a solution of 1,4-bis(2-ethylhexyloxy)benzene (9.5 g, 28 mmol) and paraformaldehyde (1.9 g) in hydrobromic acid (48%, 60 mL) and acetic acid (90 ml) was stirred for 17 h at 70°C , the solution was cooled to room temperature for 2 h. The deposited crystals were filtered and washed by water and *n*-hexane to afford 1,4-bis(2-ethylhexyloxy)-2,5-bis(bromomethyl)benzene as colorless crystals. Yield: 82% (12 g); ^1H NMR (400 MHz, CDCl_3) δ 0.89 - 0.97 (m, 12H, $-\text{CH}_3$), 1.32-1.61 (m, 16H, $-\text{CH}_2-$), 1.72-1.78 (m, 2H, $>\text{CH}-$), 3.87 (d, 4H, $-\text{CH}_2\text{O}$, $J = 5.6$ Hz), 4.52 (s, 4H, $-\text{CH}_2\text{Br}$), 6.85 (s, 2H, Ar-H). A mixture of 1,4-bis(2-ethylhexyloxy)-2,5-bis(bromomethyl)benzene (11 g, 21 mmol) and triethyl phosphite (8.8 g, 53 mmol) was stirred for 1.5 h at 130°C with removing by-product (bromoethane) using distilling receiver. The crude product was purified by column chromatography on silica gel (eluant: hexane/ethyl acetate = 5/1) to afford 1,4-Bis(2-ethylhexyloxy)-2,5-bis(diethylphosphonomethyl)benzene as a colorless liquid. Yield: 96% (13 g); ^1H NMR (400 MHz, CDCl_3) δ 0.88-0.94 (m, 12H, $-\text{CH}_3$), 1.23 (t, 12H, $-\text{OCH}_2\text{CH}_3$, $J = 7.1$ Hz), 1.29-1.56 (m, 16H, $-\text{CH}_2-$), 1.67-1.73 (m, 2H, $>\text{CH}-$), 3.22 (d, 4H, $\text{Ph}-\text{CH}_2-\text{P}$, $J = 20.2$ Hz), 3.81 (d, 4H, $-\text{OCH}_2-$, $J = 5.6$ Hz), 3.96-4.06 (m, 8H, $-\text{OCH}_2\text{CH}_3$), 6.94 (s, 2H, Ph-H). This compound was used for the preparation of the following distyrylbenzenes (**1a-g**) without further purification.

2.1.2. 1,4-Bis(2-ethylhexyloxy)-2,5-bis(*p*-dimethylaminostyryl)benzene (**1a**)

A solution of 1,4-bis(2-ethylhexyloxy)-2,5-bis(diethylphosphonomethyl)benzene (0.50 g, 0.79 mmol) and *p*-dimethylaminobenzaldehyde (2.5 g, 1.7 mmol) in tetrahydrofuran (THF) (5 mL) was added dropwise to a solution of $t\text{BuOK}$ (0.31 g, 2.8 mmol) in THF (10 mL) and stirred for 2 h at room temperature. After removal of the solvent and the addition of 1M hydrochloric acid for neutralization, the deposited crystal was filtered and washed by cooled hexane to afford yellow crystals. Yield: 54% (0.26 g); mp $159-160^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 0.92 (t, 6H, $-\text{CH}_3$, $J = 7.0$ Hz), 0.99 (t, 6H, $-\text{CH}_3$, $J = 7.5$ Hz), 1.28-1.67 (m, 16H, $-\text{CH}_2-$), 1.74-1.88 (m, 2H, $>\text{CH}-$), 2.98 (s, 12H, $-\text{N}(\text{CH}_3)_2$), 3.94 (d, 4H, $-\text{OCH}_2-$, $J = 5.5$ Hz), 6.72 (d, 4H, Ph-H, $J = 8.8$ Hz), 7.05 (d, 2H, $-\text{CH}=\text{CH}-$, $J = 16.4$ Hz), 7.09 (s, 2H, Ph-H), 7.30 (d, 2H, $-\text{CH}=\text{CH}-$, $J = 16.4$ Hz), 7.42 (d, 4H, Ph-H, $J = 8.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 11.77, 14.56, 23.55, 24.68, 29.71, 31.36, 40.26, 40.93, 72.21, 110.29, 112.95, 119.79, 127.17, 127.21, 127.89, 128.67, 150.34, 151.33; MS (m/z) 624 (M^+); Anal. Calcd for $\text{C}_{42}\text{H}_{60}\text{N}_2\text{O}_2$: C, 80.72; H, 9.68; N, 4.48. Found: C, 80.45; H, 9.87; N, 4.34.

2.1.3. 1,4-Bis(2-ethylhexyloxy)-2,5-bis(*p*-methoxystyryl)benzene (**1b**)

This compound was prepared in a manner similar to the procedure described above using 1,4-bis(2-ethylhexyloxy)-2,5-bis(diethylphosphonomethyl)benzene (0.50 g, 0.79 mmol) and *p*-anisaldehyde (2.3 g, 1.7 mmol) and ^tBuOK (0.31 g, 2.8 mmol). Yield: 39% (0.19 g) as light yellow crystals; mp 86-87°C; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (t, 6H, -CH₃, *J* = 7.1 Hz), 0.99 (t, 6H, -CH₃, *J* = 7.5 Hz), 1.30-1.65 (m, 16H, -CH₂-), 1.74-1.88 (m, 2H, >CH-), 3.82 (s, 6H, -OCH₃), 3.94 (d, 4H, -OCH₂-, *J* = 5.5 Hz), 6.90 (d, 4H, Ar-H, *J* = 8.8 Hz), 7.05-7.13 (m, 4H, -CH=CH-, Ar-H), 7.36 (d, 2H, -CH=CH-, *J* = 16.5 Hz), 7.46 (d, 4H, Ar-H, *J* = 8.7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 11.76, 14.54, 23.54, 24.68, 29.70, 31.38, 40.23, 55.73, 72.22, 110.54, 114.55, 121.91, 127.17, 128.04, 128.43, 131.36, 151.47, 159.55; MS (*m/z*) 598 (M⁺); Anal. Calcd for C₄₀H₅₄O₄: C, 80.22; H, 9.09. Found: C, 80.18; H, 9.28.

2.1.4. 1,4-Bis(2-ethylhexyloxy)-2,5-bis(*p*-methylstyryl)benzene (**1c**)

This compound was prepared in a manner similar to the procedure described above using 1,4-bis(2-ethylhexyloxy)-2,5-bis(diethylphosphonomethyl)benzene (1.0 g, 1.6 mmol) and *p*-tolualdehyde (0.40 g 3.3 mmol) and ^tBuOK (0.61 g, 5.5 mmol). Yield: 35% (0.31 g) as light yellow crystals; mp 113-114°C; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (t, 6H, -CH₃, *J* = 7.0 Hz), 0.99 (t, 6H, -CH₃, *J* = 7.5 Hz), 1.29-1.66 (m, 16H, -CH₂-), 1.75-1.87 (m, 2H, >CH-), 2.35 (s, 6H, -CH₃), 3.94 (d, 4H, -OCH₂-, *J* = 5.5 Hz), 7.07-7.14 (m, 6H, -CH=CH-, Ph-H), 7.16 (d, 4H, Ph-H, *J* = 8.1 Hz), 7.42 (d, 2H, Ph-H, *J* = 8.0 Hz), 7.45 (d, 2H, -CH=CH-, *J* = 16.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 11.78, 14.56, 21.69, 23.56, 24.70, 29.73, 31.40, 40.25, 72.24, 110.69, 123.01, 126.81127.25, 128.94, 129.81, 135.73, 137.63, 151.58; MS (*m/z*) 566 (M⁺); Anal. Calcd for C₄₀H₅₄O₂: C, 84.75; H, 9.60. Found: C, 84.59; H, 9.83.

2.1.5. 1,4-Bis(2-ethylhexyloxy)-2,5-distylylbenzene (**1d**)

This compound was prepared in a manner similar to the procedure described above using 1,4-bis(2-ethylhexyloxy)-2,5-bis(diethylphosphonomethyl)benzene (0.50 g, 0.79 mmol) and benzaldehyde (0.18 g 1.7 mmol) and ^tBuOK (0.31 g, 2.8 mmol). Yield: 50% (0.21 g) as yellow green crystals; mp 86-87°C; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (t, 6H, -CH₃, *J* = 7.0 Hz), 0.99 (t, 6H, -CH₃, *J* = 7.5 Hz), 1.30-1.66 (m, 16H, -CH₂-), 1.74-1.90 (m, 2H, >CH-), 3.96 (d, 4H, -OCH₂-, *J* = 5.5 Hz), 7.10-7.19 (m, 4H, -CH=CH-, Ph-H), 7.24 (t, 2H, Ph-H, *J* = 7.4 Hz), 7.35 (t, 4H, Ph-H, *J* = 7.6 Hz), 7.46-7.56 (m, 6H, -CH=CH-, Ph-H); ¹³C NMR (100 MHz, CDCl₃) δ 11.77, 14.55, 23.56, 24.70, 29.73, 31.40, 40.24, 72.24, 110.79, 123.98, 126.90, 127.27, 127.80, 129.09, 138.47, 151.66; MS (*m/z*): 538 (M⁺); Anal. Calcd for C₃₈H₅₀O₂: C, 84.71; H, 9.35. Found: C, 84.56; H, 9.60.

2.1.6. 1,4-Bis(2-ethylhexyloxy)-2,5-bis(*p*-chlorostyryl)benzene (**1e**)

This compound was prepared in a manner similar to the procedure described above using 1,4-bis(2-ethylhexyloxy)-2,5-bis(diethylphosphonomethyl)benzene (0.50 g, 0.79 mmol) and *p*-chlorobenzaldehyde (0.23 g 1.7 mmol) and ^tBuOK (0.31 g, 2.8 mmol). Yield: 43% (0.20 g) as yellow green crystals; mp 104-106°C; ¹H NMR (400 MHz, CDCl₃) δ 0.91 (t, 6H, -CH₃, *J* = 7.0 Hz), 0.99 (t, 6H, -CH₃, *J* = 7.5 Hz), 1.28-1.65 (m, 16H, -CH₂-), 1.75-1.85 (m, 2H, >CH-), 3.94 (d, 4H, -OCH₂-, *J* = 5.5 Hz), 7.03-7.14 (m, 4H, -CH=CH-, Ph-H), 7.31 (d, 4H, Ph-H, *J* = 8.5 Hz), 7.39-7.50 (m, 6H, -CH=CH-, Ph-H); ¹³C NMR (100 MHz, CDCl₃) δ 11.76, 14.55, 23.54, 24.69, 29.70, 31.40, 40.20, 72.23, 110.77, 124.55, 127.11, 127.94, 128.01, 129.25, 133.35, 136.95, 151.67; MS (*m/z*) 606 (M⁺); Anal. Calcd for C₃₈H₄₈Cl₂O₂: C, 75.10; H, 7.96. Found: C, 74.97; H, 8.07.

2.1.7. 1,4-Bis(2-ethylhexyloxy)-2,5-bis(*p*-cyanostyryl)benzene (**1f**)

This compound was prepared in a manner similar to the procedure described above using 1,4-bis(2-ethylhexyloxy)-2,5-bis(diethylphosphonomethyl)benzene (0.50 g, 0.79 mmol) and *p*-cyanobenzaldehyde (0.21 g 1.6 mmol) and ^tBuOK (0.31 g, 2.8 mmol). Yield: 54% (0.25 g) as light orange crystals; mp 160-161°C; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (t, 6H, -CH₃, *J* = 7.0 Hz), 1.00 (t, 6H, -CH₃, *J* = 7.5 Hz), 1.30-1.64 (m, 16H, -CH₂-), 1.76-1.89 (m, 2H, >CH-), 3.97 (d, 4H, -OCH₂-, *J* = 5.5 Hz), 7.12 (s, 2H, Ph-H), 7.17 (d, 2H, -CH=CH-, *J* = 16.5 Hz), 7.52-7.68 (m, 10H, -CH=CH-, Ph-H); ¹³C NMR (100 MHz, CDCl₃) δ 11.74, 14.52, 23.51, 24.69, 29.67, 31.38, 40.14, 72.18, 110.79, 119.51, 127.12, 127.20, 127.50, 127.72, 132.90, 142.82, 151.93; MS (*m/z*) 588 (M⁺); Anal. Calcd for C₄₀H₄₈N₂O₂: C, 81.59; H, 8.22; N, 4.76. Found: C, 81.33; H, 8.35; N, 4.74.

2.1.8. 1,4-Bis(2-ethylhexyloxy)-2,5-bis(*p*-nitrostyryl)benzene (**1g**)

This compound was prepared in a manner similar to the procedure described above using 1,4-bis(2-ethylhexyloxy)-2,5-bis(diethylphosphonomethyl)benzene (0.50 g, 0.79 mmol) and *p*-nitrobenzaldehyde (0.25 g 1.6 mmol) and ^tBuOK (0.31 g, 2.8 mmol). Yield: 24% (0.12 g) as red crystals; mp 160-161°C; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (t, 6H, -CH₃, *J* = 7.0 Hz), 1.01 (t, 6H, -CH₃, *J* = 7.5 Hz), 1.30-1.64 (m, 16H, -CH₂-), 1.80-1.91 (m, 2H, >CH-), 3.99 (d, 4H, -OCH₂-, *J* = 5.5 Hz), 7.14 (s, 2H, Ph-H), 7.23 (d, 2H, -CH=CH-, *J* = 16.5 Hz), 7.55-7.74 (m, 6H, -CH=CH-, Ph-H), 8.23 (d, 4H, Ph-H, *J* = 8.8 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 11.74, 14.51, 23.50, 24.69, 29.66, 31.38, 40.14, 72.18, 111.01, 124.60, 127.17, 127.21, 127.41, 128.40, 144.82, 147.07, 152.03; MS (*m/z*) 628 (M⁺). Although all spectra show the appropriate data for this compound, the satisfactory elemental analysis was not obtained.

2.2 Fluorescence quantum yields of the DSBs (**1a-g**)

9,10-Diphenylanthracene was used as a standard [$\Phi_F = 1.00$ in cyclohexane: Lit. G. Heinrich, S. Schoof, H. Gusten, J. Photochem. 3 (1974/75) 315-320)] by excitation at 375 nm. All DSBs and 9,10-diphenylanthracene (DPA) were dissolved in cyclohexane at 10^{-6} M and measured their absorptions at 375 nm. Thus obtained absorptions (Abs) and the integrated areas (S) of the emission spectra obtained by excitation at 375 nm were used for estimation of the fluorescence quantum yields according to the following equation (a term for the index of refraction is omitted because of the measurements in the same solvent).

$$\Phi_{F\text{ DSB}} / \Phi_{F\text{ DPA}} = S_{\text{DSB}} \times \text{Abs}_{\text{DPA}} / S_{\text{DPA}} \times \text{Abs}_{\text{DSB}}$$

The relative fluorescence quantum yields in aqueous THF (THF/H₂O = 3/1) were estimated in a manner similar to the above using **1d** (R = H) as a standard. These values are listed in Table 2.

2.3. Measurement of Φ_{CL}

For a typical run, 0.5 mL of a solution containing sodium carbonate (4.0×10^{-4} M) and hydrogen peroxide (1.0×10^{-2} M) in distilled water was added to 1.5 mL of a solution containing the oxalates (5.0×10^{-6} M) and fluorophores (1.0×10^{-5} M) in THF in a quartz cell placed in front of the photomultiplier at 25°C. The photons generated were counted with the photomultiplier. The average of the values obtained by three times measurements was used for the calculation of Φ_{CL} .

3. Results and discussion

3.1. Spectral data of distyrylbenzene (DSB) fluorophores

DSB fluorophores **1a-g** with 2-ethylhexyloxy groups at the center of the molecules for increasing their solubility in organic solvents and with various substituents at the *para*, *para'*-positions were prepared via the Horner-Wadsworth-Emmons reaction of the bisphosphonate and the corresponding aromatic aldehydes. The absorption and fluorescence spectra measured in aqueous THF are shown in Fig. 1, and the spectral data measured both in aqueous THF (THF/H₂O=3/1) and cyclohexane are summarized in Table 2. The Hammett substituent constants (σ_p^+) of the DSBs are also included in Table 2. DSBs **1b-1e** show absorption maxima around 390 nm and the emissions around 450 nm, while **1a**, **1f** and **1g** with strongly electron-donating or attracting substituents show some red-shifts

in both spectra compared to the others. The fluorescence quantum yields (Φ_F) of **1a-f** in cyclohexane have similar values, and **1g** (R=NO₂) showed a much lower Φ_F compared to the others. For CL study, the *rel.* Φ_S in aqueous THF were also measured and **1g** was found to be almost non-fluorescent [42] probably due to the loss of the excitation energy through the hydrogen bonds of the nitro groups in protic media.

3.2. DSB enhanced PO-CL reactions of the eight oxalates and the Hammett correlation between the DSB substituents and the relative singlet chemiexcitation yields

When TCPO was reacted with alkaline hydrogen peroxide in the presence of **1a** or **1b** in aqueous THF, an intense CL was observed, whose spectra were in agreement with the fluorescence spectra of **1a** and **1b** (Fig. 2). This indicated that the emitting species are the excited **1a** and **1b** generated during the reactions as reported in the previous reports, in which the PO-CL reactions of the several oxalates and oxamates were enhanced by the various fluorescent DSBs in a bimolecular manner, and the CL quantum yields (Φ_{CL}) were related to the electronic nature of the DSBs [38,39].

All the PO-CL reactions using the oxalates listed in Table 1 were completed within a few seconds under the prescribed conditions for the present study and provided various total CL quantum yields (Φ_{CL}) depending on the type of oxalates and fluorophores (Table 3). Since the PO-CL reaction in the aqueous media is accompanied by hydrolysis of the oxalates to form the oxalic acids and phenols, a large excess amount of hydrogen peroxide (ca. 700 times vs. the oxalates) was used to undergo the peroxalate reactions before hydrolysis.

The Φ_{CL} was highly dependent on the electronic nature of fluorophores in the previously investigated PO-CL reactions, and, therefore, a Hammett correlation between the Φ_{CL} and the DSB substituent constants would give the useful information for the chemiexcitation of the DSBs as well as the information of the HEIs because the DSBs would electronically interact with the HEIs to form the polarized complexes initially as the precursors of the radical ion pairs according to the CIEEL mechanism. The relative singlet chemiexcitation yield (*rel.* Φ_S defined as $\Phi_{CL}/\text{rel. } \Phi_F$) for each CL reaction was correlated with the DSB substituent constants (σ_p^+) in terms of the Hammett relationship; namely, the plots of σ_p^+ -values versus $\log (\Phi_S/\Phi_{S(H)})$ for all the PO-CL reactions gave straight lines with negative slopes (ρ -values) as shown in Fig. 3. The σ_p^+ values were used as the substituent constants for the examination of the present Hammett correlation because the DSBs would interact with electron deficient HEIs to form the positively charged DSBs that would be stabilized with electron-donating substituents by the resonance effect. However, the DSB **1a** and **1g** could not be applied to the examination of this Hammett correlation because the former produced

too high a Φ_{CL} value that exceeded the limit of the photon-counting system set for this study and the latter was almost non-fluorescent under these CL conditions. It is interesting to note that the ρ -values for the eight oxalates in Table 4 are apparently classified into three groups by their ranges, i) the smallest value of -1.01 for DNPO, ii) between -0.9 and -0.8 for 2,4-DCPO, 2-CPO, 4-CPO, 4-CPPO and DPO, and iii) near -0.6 for TCPO and 2,6-DCPO. The salient feature of these ρ -values is that the highly activated DNPO had the highest absolute ρ -values, but two oxalates, TCPO and 2,6-DCPO, had the lowest values. Because the pK_a values of the phenols [43,44] are the tentative indicators of their electronic nature, the pK_a of the phenols forming the oxalates (Table 1) are also related to the ρ -values as shown in Fig. 4, in which the oxalates consisting of strongly acidic phenols tend to produce high absolute ρ -values except for TCPO and 2,6-DCPO.

The CL decay curves of the PO-CL enhanced by **1b** as the representative fluorophore are shown in Fig. 5a and well fitted by the single exponential decay as shown in Fig. 5b as has been observed for the typical PO-CL [12,13,45]. The pseudo-first-order decay rate constants (k) estimated from the logarithmic plots of the decay curves (Fig. 5b) are listed in Table 4. The rate-determining step for the formation of the HEIs will be the bimolecular process in which an oxalates reacts with perhydroxy anion to give hydroperoxide because the CL decay rates are dependent on the phenol acidity (Fig. 6) except for TCPO and 2,6-DCPO with much lower CL decay rates [22]. The observed correlation between k and pK_a is similar to that between $|\rho|$ and pK_a (Fig. 4). The deviation for TCPO and 2,6-DCPO is probably due to the steric effect of the *ortho*-phenol substituents on the both initial and the subsequent intramolecular acyl substitutions to form the cyclic HEIs [45].

3.3. Evaluation of the Hammett correlation providing various ρ -values and explanation by the frontier molecular orbital (FMO) theory

As observed in the experimental results, various ρ -values with a relatively large range were produced depending on the oxalate structures, which suggests that the initial electronic interaction is a rate-limiting process for the chemiexcitation step and the reactive oxalates would give the polar species in the electronic interaction between the HEI and the DSBs. Since the electronic interaction is much faster than the chemical reactions forming the HEI and cannot be kinetically observed as has been documented [3,6,14,17], the ρ -value will be related to the electronic interaction between the HEI and the fluorophores. For the high absolute ρ -value, the preferable electronic interaction would promote the electron exchange process to form a radical ion pair of the DSB radical cation and carbon dioxide radical anion in the CIEEL process. It should be noted that the formation of the excited DSBs is the result of the back electron transfer from the radical anions to the DSB radical

cations, but the present study applying the Hammett correlation focuses on the initial stage of the electronic interaction between the HEIs and the DSBs, which, however, controls the DSB chemiexcitation as a result.

A possible explanation for various ρ -values in the Hammett correlation in the present PO-CL system is based on diversity of the HEIs electronically interacting with the DSBs; the oxalates with the higher ρ -values form HEIs which make effective electronic interactions. The strength of the electronic interactions depends on the oxalate structures, to indicate that HEIs retain the phenol moieties. Thus, DOD is excluded as a HEI. The DOT intermediates with the phenol ester moieties are, in principle, capable of generating excited fluorophores by an electronic interaction with the fluorophores [19] considering the structural similarity to the chemiluminescent α -peroxy lactones [46]. The same ρ -value for DPO and 4-CPPO is probably due to the structurally same HEIs, because 4-CPPO would eliminate the 4-chlorophenol by the initial nucleophilic acyl substitution leading to the formation of an intermediate the same as that formed from DPO.

The relative heats of formation of the phenyl *O,O*-hydrogen monoperoxalate, the HEIs, such as the DOT together with DOD, and the final products, such as carbon dioxide and phenol, calculated by *ab initio* method using the B3LYP/6-31G (d) basis set, are shown in Fig. 7 as examples. The formation of the cyclic peroxides, the HEIs from the acyclic hydroperoxide, is an endothermic process, while their decomposition to carbon dioxide and phenol is a very favorable exothermic process. It is noteworthy that the conversion from the DOT to the DOD is an endothermic process with a small energy difference (4.64 kcal/mol), which slightly favors the DOT at equilibrium, and the DOT can be a candidate for the HEI more than DOD.

The Hammett substituent constants are also regarded as the index of the electron releasing ability and parallel to the oxidation potentials of the compounds bearing the Hammett substituents. Therefore, the Hammett relationship has been applied to explain the substituent effect on the electron transfer [47-50]. The Hammett correlation also has been rationalized with the FMO theory [51], in which the magnitudes of the ρ -values are closely related to the energy gaps between the HOMOs and LUMOs of the electron-donor and electron-acceptor, respectively. When two molecular orbitals interact, the smaller the interval between the FMO energies, the higher the interaction energy becomes. The small difference in the energy gap of the FMOs leads to increase contribution of the electronic effect on the reaction process, resulting in the higher ρ -values. This treatment with the FMO theory for the electronic interaction between the HEI and the DSBs corresponds to the analysis with CIEEL mechanism. As the negative sign of the ρ -values in the present PO-CL system indicates the interaction of the DSB-HOMOs and DOT- or DOD-LUMOs, the FMO theory predicts that the lower LUMO energies of DOT leads to the smaller energy difference between their LUMOs and the DSB-HOMOs in the endothermic electron transfer,

resulting in the significant change in the electronic interaction rates along with the changes in the σ_p^+ -values, and finally increasing the absolute ρ -values.

The energies of the DSB-HOMOs and the DOT-LUMOs as well as the DOD-LUMO were also calculated and their energy levels and the representative orbital shapes are shown in Fig. 8. For the DOT produced from DNPO, the LUMO+2 was selected as the orbital interacting with the DSBs because its LUMO and LUMO+1 are localized at the phenyl ring bearing two nitro groups. For all the DOTs (LUMO+2 for the DOT from DNPO), the LUMOs extend on the O-O bondings, which is reasonable for the proposed CIEEL process that begins with an electron transfer from the fluorophores to the anti-bonding orbitals of the DOTs. There is a remarkable difference in the shapes of the LUMOs of the DOTs and DOD, the former of which is anti-bonding but the latter of which is bonding, but both HEIs are ready to accept an electron as revealed by the extending LUMOs on the O-O bondings. If both HEIs hold an electron to form their radical anions, the O-O bond cleavage will readily take place. Fig. 9 shows the relationship between the ρ -values and the LUMO energies of the DOTs, in which the oxalates with the higher absolute ρ -values tend to have lower LUMO energies except for TCPO and 2,6-DCPO. This tendency agrees with the prediction by the FMO theory, if the DOT is involved in the electronic interaction during the CIEEL process. On the other hand, the deviation by TCPO and 2,6-DCPO is also significant because they would give much higher ρ -values from the viewpoint of the FMO theory conflicting with the experimental observation. The steric hindrance in the HEIs would not only decrease the CL decay rate but also restrain the electronic interactions with the DSBs, which also correlates with the importance of the DOTs as the HEIs because such results would be expected for the aryl group containing HEIs. When the DOTs electronically interact with the fluorophores, it would be possible that the DOT radical anions decompose into phenols and CO₂ including its radical anions because the σ^* bonding of the DOT occupied with an electron readily breaks resulting in a ring cleavage as shown in Scheme 2.

5. Conclusions

In the present PO-CL reactions using several oxalates and the DSB fluorophores, the linear Hammett correlations with various ρ -values between the singlet chemiexcitation yields and the DSB substituent constants (σ_p^+) were established, and the ρ -values were related to the CL decay rates and LUMO energies of the postulated HEIs such as the DOTs. The FMO theory explains the experimental observations by the reason that the electronic interaction operates with various biases depending on the oxalate structure and that the donor-acceptor electronic interaction determines the

ρ -value.

Acknowledgements

This work was supported by the Global COE from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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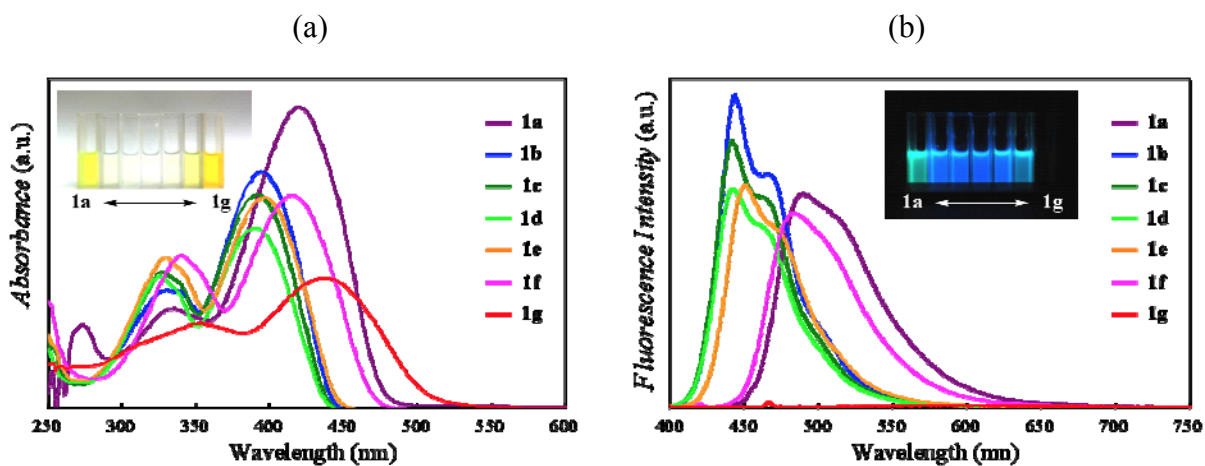


Fig. 1. Absorption (a) and fluorescence (b) spectra of the DSBs **1a-g**. 7.5×10^{-6} M in THF/H₂O (3:1).

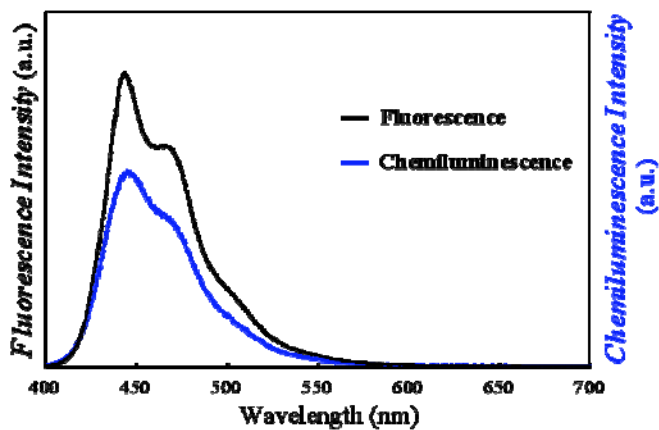


Fig. 2. Fluorescence and chemiluminescence spectra of **1b** using TCPO. Oxalate (7.5×10^{-5} M), DSB derivatives (7.5×10^{-6} M) and H₂O₂ (2.5×10^{-1} M) in THF/H₂O (3:1) were used.

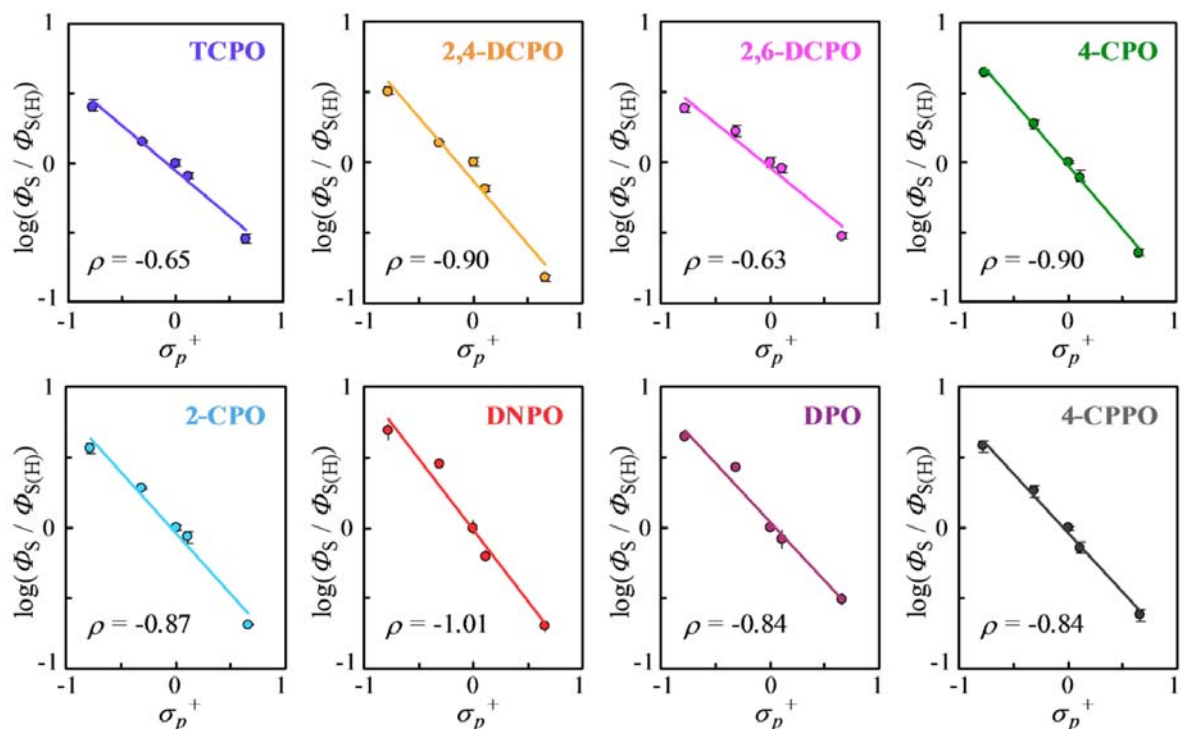


Fig. 3. The Hammett correlation of PO-CL of the eight oxalates enhanced by DSBs (**1b-f**). [oxalates]= 3.75×10^{-6} M, [DSBs]= 7.5×10^{-6} M, [H_2O_2]= 2.5×10^{-3} M, and [Na_2CO_3]= 7.5×10^{-5} M in THF/ H_2O (3/1).

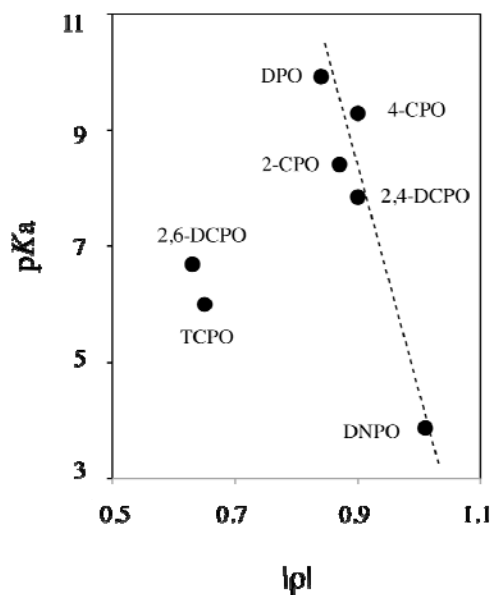


Fig. 4. Correlation of pKa of phenols in the oxalates and ρ -values.

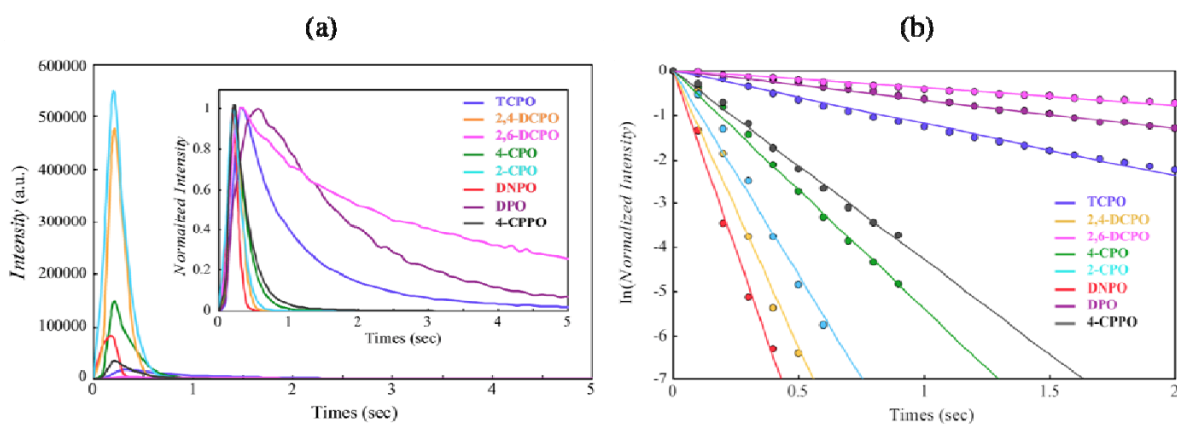


Fig. 5. The CL decay curves and logarithm plots of the eight oxalates using **1b** as the fluorophore: (a) CL decay curves (inset: normalized curves), (b) pseudo-first-order reaction fitting of the normalized CL emission decays. [oxalate]= 3.75×10^{-6} M, [**1b**]= 7.5×10^{-6} M, [H_2O_2]= 2.5×10^{-3} M, and [Na_2CO_3]= 7.5×10^{-5} M in THF/ H_2O (3/1). Standard deviations (R^2): 0.990 for TCPO, 0.995 for 2,4-DCPO), 0.979 for 2,6-DCPO, 0.994 for 4-CPO, 0.979 for 2-CPO, 0.992 for DNPO, 0.996 for DPO, 0.994 for 4-CPPO.

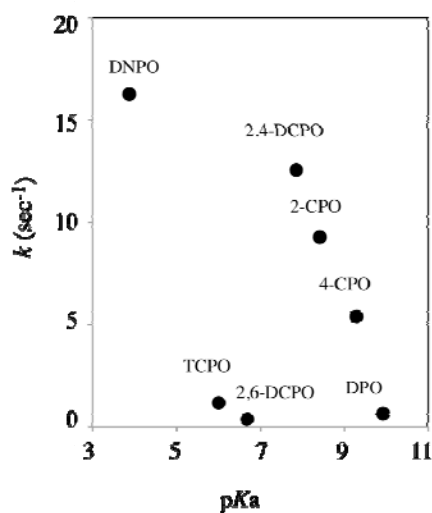


Fig. 6. Correlation of the CL decay rates (k) and $\text{p}K_a$ of phenols in the oxalates.

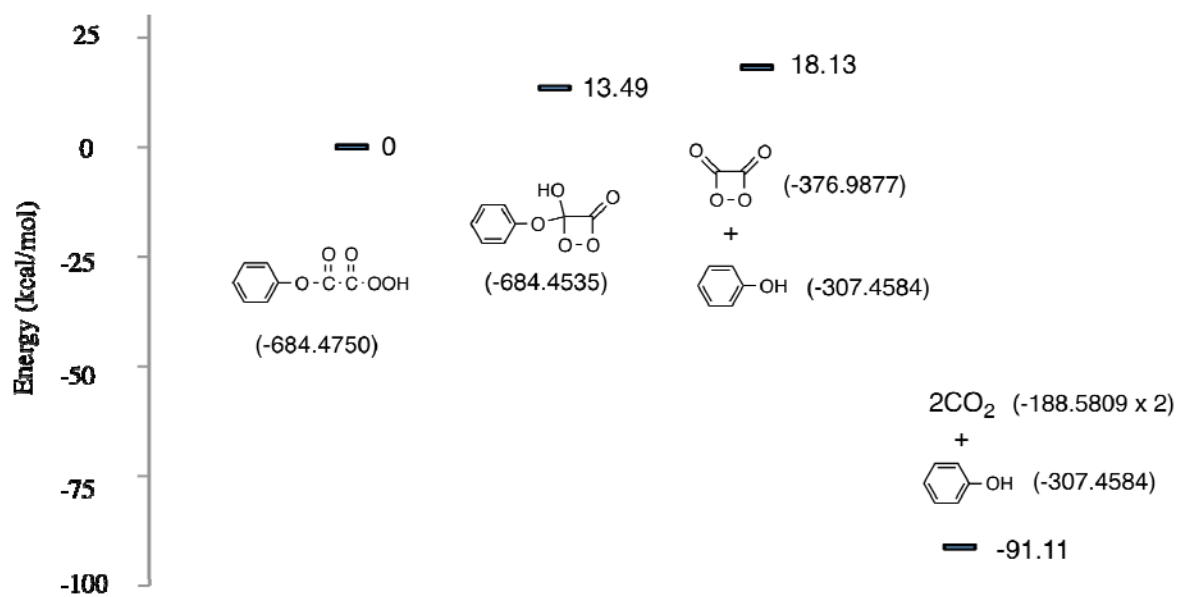


Fig. 7. Relative heats of the formation of the high-energy intermediates and its decomposition. The values in parentheses are the energies in atomic unit (Hartree) calculated by the *ab initio* method with a B3LYP/6-31g(d) basis set.

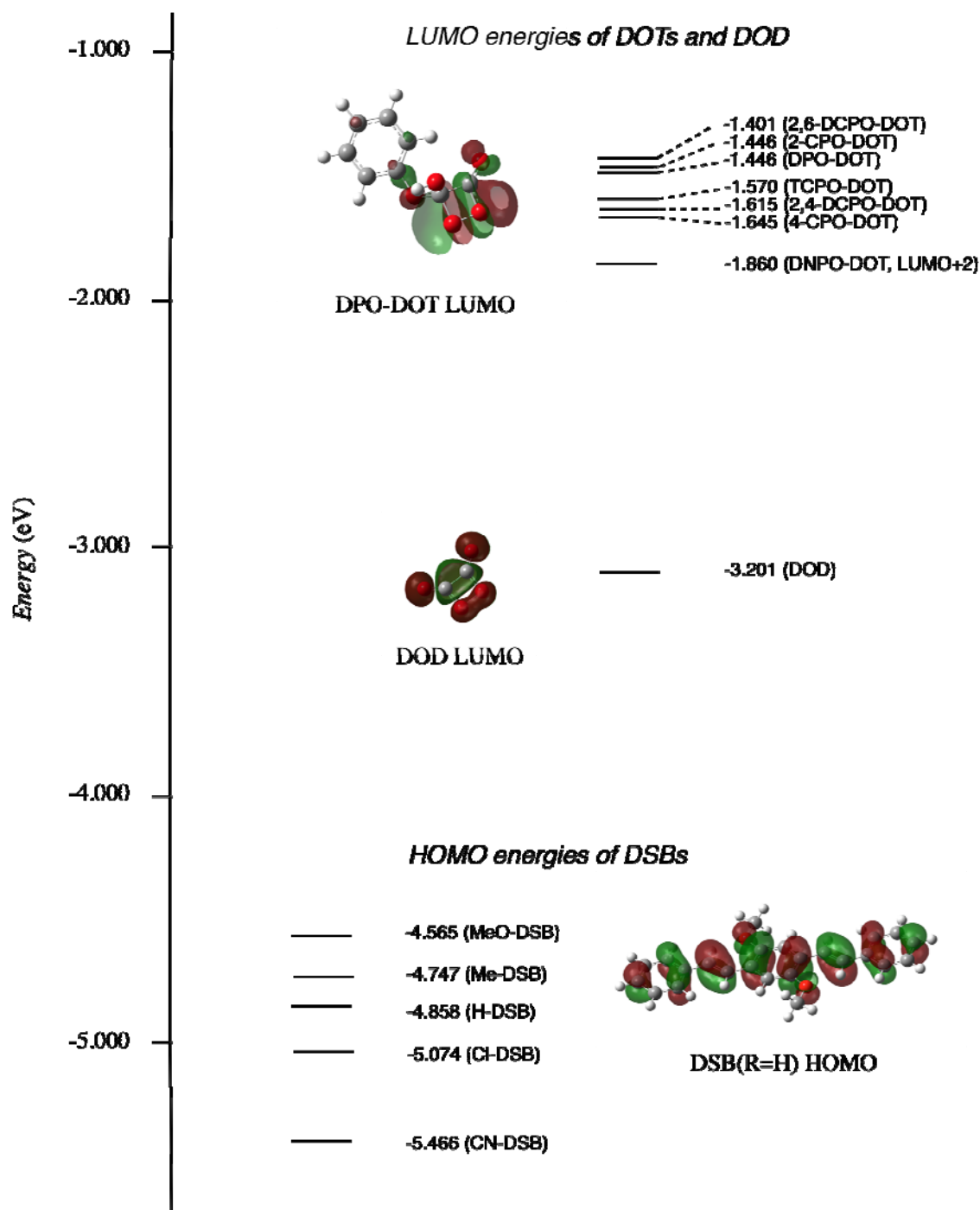


Fig. 8. The HOMO (DSBs) and LUMO (DOTs and DOD) energies. Calculated by the *ab initio* method with a B3LYP/6-31g(d) basis set.

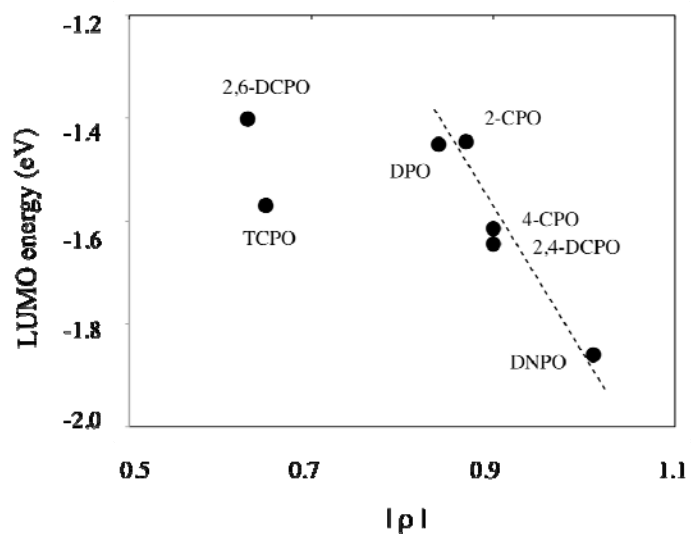


Fig. 9. Plots of absolute ρ -value vs. LUMO energy.

Table 1

Structures of oxalates used in this study and pKa of phenols as leaving groups.

Oxalate	Abbreviation	X ₁	X ₂	X ₃	pKa of phenol
diphenyl oxalate	DPO	H	H	H	9.91
bis(2,4,6-trichlorophenyl) oxalate	TCPO	Cl	Cl	Cl	6.00
bis(2,4-dichlorophenyl) oxalate	2,4-DCPO	Cl	Cl	H	7.85
bis(2,6-dichlorophenyl) oxalate	2,6-DCPO	Cl	H	Cl	6.69
bis(4-chlorophenyl) oxalate	4-CPO	H	Cl	H	9.29
bis(2-chlorophenyl) oxalate	2-CPO	Cl	H	H	8.41
bis(2,4-dinitrophenyl) oxalate	DNPO	NO ₂	NO ₂	H	3.87
4-chlorophenyl phenyl oxalate	4-CPPO				-

Table 2The Hammett substituent constants (σ_p^+) and spectral data of distyrylbenzenes (DSBs).^a

DSBs	R	σ_p^+	λ_{vis} (nm) ^a	λ_{em} (nm) ^a	Φ_F ^b	rel. Φ_F in aq. THF ^{a,c}
1a	NMe ₂	-1.70	419	490 (441)	0.73	1.32
1b	OMe	-0.778	394	444(395)	0.78	1.32
1c	Me	-0.311	391	442(340)	0.75	1.16
1d	H	0	390	442(390)	0.76	1.00
1e	Cl	0.114	396	451(397)	0.81	1.03
1f	CN	0.659	415	484(424)	0.70	1.10
1g	NO ₂	0.790	444	556(452)	0.25	0.04

^a Measured in THF/H₂O (3/1) (7.5×10⁻⁶ M). ^b Measured in cyclohexane using 9,10-diphenylanthracene as a standard. ^c Relative values based on the Φ_F for **1d**.

Table 3 Chemiluminescence quantum yields ($\Phi_{\text{CL}} \times 10^4$) of the PO-CL for eight oxalates enhanced by DSBs (**1b-f**).^a

DSB	TCPO	2,4-DCPO	2,6-DCPO	4-CPO	2-CPO	DNPO	DPO	4-CPPO
1b (R=OMe)	1.12	6.30	1.01	3.63	8.68	1.06	0.29	0.72
1c (R=Me)	0.55	2.38	0.61	1.36	3.97	0.54	0.16	0.30
1d (R=H)	0.33	1.50	0.32	0.62	1.79	0.17	0.05	0.14
1e (R=Cl)	0.27	1.00	0.29	0.50	1.58	0.11	0.04	0.11
1f (R=CN)	0.11	0.25	0.10	0.15	0.41	0.04	0.02	0.04

^a [oxalate]= 3.75×10^{-6} M, [DSB]= 7.5×10^{-6} M, [H₂O₂]= 2.5×10^{-3} M, [Na₂CO₃]= 7.5×10^{-5} M.

Table 4

The ρ -values and the pseudo-first-order rate constants of the CL decays of the eight oxalates enhanced by **1b**.

oxalate	ρ -value	pseudo-first-order decay rate ^a k (sec ⁻¹)
TCPO	-0.65	1.18
2,4-DCPO	-0.90	12.56
2,6-DCPO	-0.63	0.38
4-CPO	-0.90	5.40
2-CPO	-0.87	9.28
DNPO	-1.01	16.27
DPO	-0.84	0.65
4-CPPO	-0.84	4.28

^a Standard deviations (R^2) are described in Fig. 5.