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Peroxyoxalate Chemiluminescence of *N*,*N*′-Bistosyl-1*H*,4*H*-quinoxaline-2,3-dione and Related Compounds. Dependence on Electronic Nature of Fluorophores

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The title compound *N*,*N*′-bistosyl-1*H*,4*H*-quinoxaline-2,3-dione (TsQD) provides peroxyoxalate chemiluminescence (PO-CL) when reacted with hydrogen peroxide in the presence of fluorophores. The chemiluminescence (CL) efficiency of TsQD was superior to that of other related compounds such as bis(2,4,6-trichlorophenyl) oxalate (TCPO), a typical oxalate for the peroxyoxalate PO-CL, under an aqueous condition. Factors affecting the PO-CL efficiency are discussed from the viewpoint of the structures of the substrates and the electronic nature of the fluorophores. A linear correlation of the logarithmic values evaluated from the CL quantum yields with the oxidation potentials of the aromatic fluorophores supports the involvement of the chemically initiated electron exchange luminescence (CIEEL) mechanism in both TsQD- and TCPO-CL systems. Also, an excellent Hammett relationship was derived from the correlation between the σ^+ values and the relative singlet excitation yields in TsQD-CL enhanced by a series of fluorescent para,para′-disubstituted distyrylbenzenes.

Introduction

Chemiluminescence (CL) is a phenomenon in which chemically generated molecules in excited states liberate energy with light emission, which is generally accompanied by decomposition of organic peroxides.[1,2] Among several categories of chemiluminescent organic compounds, some reactive oxalates generate the most effective CL by reaction with hydrogen peroxide in the presence of various fluorophores, which is called the peroxyoxalate CL (PO-CL)[3] and is being put to practical use. Commercially available bis(2,4,6-trichlorophenyl) oxalate (TCPO) [4] is a representative example for the PO-CL. On the other hand, several oxamides or oxanilides were also found to provide CL, a few of which were superior to oxalates such as TCPO.[5−7] Since Chandoross[8] discovered the first PO-CL arising from the reaction between oxalyl chloride and hydrogen peroxide in the presence of anthracene, many reports treating the interesting luminescent reactions of oxalates have appeared. Although the reaction mechanism of PO-CL is still under controversy,[9] it is believed that their light emission is ascribed to the chemically induced electron exchange luminescence (CIEEL) mechanism.[10] However, there have been only a few investigations of the CIEEL mechanism in PO-CL despite numerous reports on this issue of isolated organic peroxides.[10,11] The examples demonstrating the CIEEL mechanism of the PO-CL from a correlation with the oxidation potentials of the fluorophores have been reported by Birks [12] and by Palmer,[13] independently. Recently, Baader et al.[14] have reported a different approach on this subject. We report in this paper

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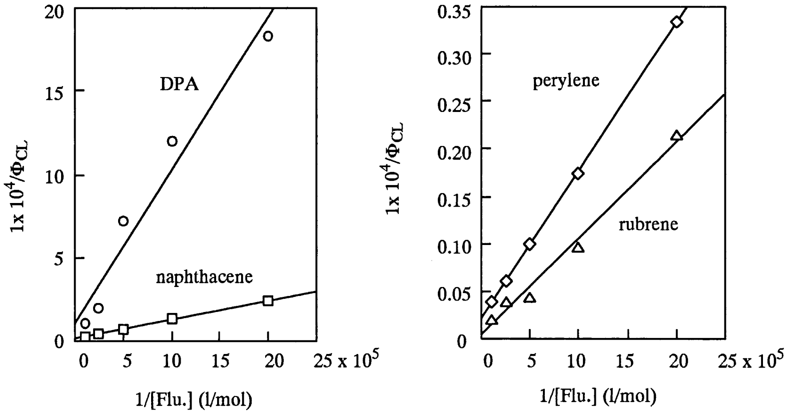
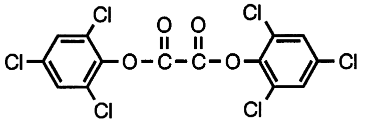
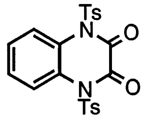


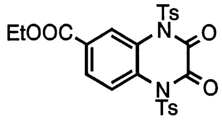
FIGURE 1. Double-reciprocal plot of the enhanced CL quantum yield (Φ_{CL}) against flurophore concentration: [TsQD] = 5×10^{-6} M in THF, [H_2O_2] = 1.5×10^{-4} M in H_2O.

that the cyclic oxamides, *N*,*N*′-bistosyl-1*H*,4*H*-quinoxaline-2,3-dione (TsQD) and its derivative with an ester group (TsQDEs), produce CL in a way similar to that of the PO-CL. The basis of the involvement of the CIEEL mechanism in the present TsQD-CL is also given.



TCPO





Ts = *p*-$CH_3C_6H_4SO_2$

TsQD **TsQDEs**

Results and Discussion

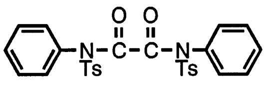
The reaction of *N*,*N*′-bistosyl-*o*-phenylenediamine and oxalyl chloride in the presence of triethylamine gave TsQD in 54% yield, and another compound bearing an ester group, TsQDEs, was prepared by a similar manner. These compounds provided very weak CL when treated with hydrogen peroxide in aqueous THF, forming *o*-phenylenediamine quantitatively along with the loss of carbon dioxide. In contrast, an enhanced CL was observed by the addition of fluorophores such as 9,10-diphenylanthracene (DPA) (blue), perylene (bright blue), naphthacene (green-blue) and rubrene (yellow). Agreement of the emission spectra with the fluorescence spectra of the addends shows that the emission is ascribed to the excited fluorophores. Addition of a base such as potassium carbonate or sodium salicylate shortened the emission time with an increase in the emission intensity. The CL quantum yields at the prescribed concentration of TsQD, hydrogen peroxide, and fluorophores were estimated by the photocounting method using luminol CL as a standard.[15] The reciprocal of the CL quantum yields is a linearly increasing function of the reciprocal of each fluorophore concentration as shown in Figure 1, which demonstrates that this CL is the result of the bimolecular interaction between the highly energetic intermediates and the fluorophores.

TABLE 1. Perylene-Enhanced CL Quantum Yields^{a,b} of TCPO, TsQD, and Related Compounds

reactant	$\Phi_{CL}^{perylene} \times 10^3$
TCPO	2.87 (21.1)^c
TsQD	16.2 (2.74)^c
TsQDEs	13.0
PhTsNCOCONTsPh (**1**)	0.000072
PhTsNCOCOOTCP (**2**)	0.24

^{a} [Reactant] = 1.0×10^{-5} M in THF, [perylene] = 2.0×10^{-4} M in THF, [H_2O_2] = 3.0×10^{-1} in H_2O. ^{b} Einstein/mol. ^{c} [reactant] = 1.0×10^{-5} M in dimethyl phthalate, [H_2O_2] = 3.0×10^{-1} M in H_2O/^{t}BuOH.

To explore the structural factor determining the CL efficiency, the related compounds **1** and **2** were prepared, and their perylene-enhanced CL quantum yields were measured. As shown in Table 1, TsQD and TsQDEs were found to be more chemiluminescent than TCPO under the present condition (THF−H_2O), but the CL quantum yields were changed under different conditions; namely, TCPO was more effective by ca. 10 times than TsQD in a mixed solvent of dimethyl phthalate and *t*-BuOH, a suitable condition for TCPO-CL.[9e] Bis(*N*-tosyl)oxanilide (**1**), an acyclic oxamide structurally close to TsQD, was much less luminescent than TsQD and also than oxamoylformate (**2**) having a hybrid structure of TCPO and **1**. This is a result of the different abilities of the eliminating groups in the first substitution with a hydroperoxy group. After **1** was reacted with hydrogen peroxide for 3 h, its conversion into *N*,*N*′-bistosyl-*o*-phenylene diamine was only 4%. In contrast, monitoring by ^{1}H NMR revealed



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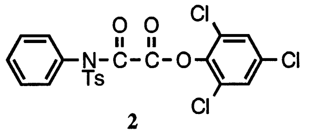

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TABLE 2. Normalized CL Quantum Yields of TsQD- and TCPO-CL Enhanced by Fluorophores with Various Oxidation Potentials

		$\Phi_{CL}^{fluor} \times 10^4/\Phi_F$ [a]		
fluorophore	Φ_F	TsQD	TCPO	E_{oxid} [b]
DPA	1.00	4.7	0.23	1.22
perylene	0.94	29.0	3.0	1.00
naphthacene	0.21	49.0	3.3	0.95
rubrene	0.98	68.0	5.4	0.82

[a] [TsQD], [TCPO] = 5.0×10^{-6} M in THF, [H_2O_2] = 1.5×10^{-1} M in H_2O, [fluor] = 1.0×10^{-4} M in THF. [b] Reference 11b.

that ca. 40 mol % of **2** decomposed into an equimolar amount of 2,4,6-trichlorophenol and *N*-tosylanilide during 2 h. No observation of an intermediate[9a,d] such as PhTsNCOCOOH in this reaction suggests that the second intramolecular substitution of a tosylanilide moiety of **2** is much easier than the first substitution of the tosylanilide moiety of **1**. Thus, the CL efficiency is chiefly dependent on the rate of the first substitution. On the other hand, **2** is less effective than TCPO, which suggests that the rate of the second intramolecular substitution step also controls the CL efficiency because the first eliminating group is a common 2,4,6-trichlorophenoxy group in both compounds. Previously, it was suggested[5] that the emission efficiencies of several oxanilides depend on the rate of the second intramolecular nucleophilic displacement of the leaving group. Consequently, a higher emission efficiency of TsQD would be due not only to acceleration of the first intermolecular nucleophilic acyl substitution but also to the activation of the second intramolecular nucleophilic attack of a peroxide anion, which is ascribed to the cyclic structure of TsQD.

Although which species (dioxetane) interacts with a fluorophore to produce light emission has not been strictly elucidated, PO-CL is believed to involve the CIEEL mechanism. The contribution of the CIEEL process is generally verified by the relationship between the emission efficiencies and the oxidation potentials of the fluorophores.[10] This operation has been applied to the PO-CL systems.[12-14] We investigated the present TsQD- as well as TCPO-CL according to the kinetic treatment used for bis(pentachlorophenyl) oxalate-CL by Palmer et al.[13] The relationship among the CL quantum yield ($\Phi_{CL}{}^F$), the oxidation potential (E_{oxid}) of a fluorophore (electron donor), the reduction potential (E_{red}) of a high energy intermediate (electron acceptor), and the Coulombic attractive stabilization (E_{coul}) of the charged ions is expressed by the following equation

$$\ln [(\Phi_F\, \Phi_{CT}'/\Phi_{CL}{}^F) - 1] = \ln(k/A[F]) + (E_{oxid} - E_{red} - E_{coul})/RT$$

where Φ_F is the fluorescence quantum efficiency, Φ_{CT}' the value dependent on the charge-transfer excited-state yield estimated from the total CL quantum yield at infinite concentration of the fluorophore (0.016 as estimated from the intercept for rubrene-enhanced CL described in Figure 1), k the rate of nonluminescent decay of a high energy intermediate, A the coefficient induced by the Weller rate law for an electron exchange, and [F] the concentration of the fluorophore. This equation describes that the left term involving the quantum yield is a linear function of E_{oxid} because other parameters can be regarded as constants in this system. Collected data for TsQD- and TCPO-CL and the plots of the evaluated left term against E_{oxid} of each fluorophore are shown in Table 2 and Figure 2, respectively. A linear correlation in both CL systems is shown, which supports involvement of a CIEEL process.

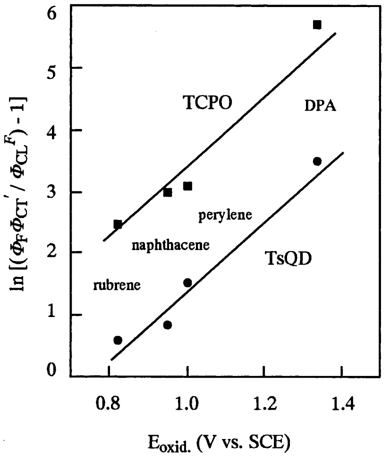


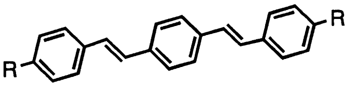
FIGURE 2. Relationship between CL quantum yield and oxidation potential of the fluorophores in TsQD- and TCPO-CL systems.

TABLE 3. Relative CT Efficiency of TsQD-CL Enhanced by Para,Para′-Disubstituted Distyrylbenzenes[a]

distyryl-benzene						
	R	rel Φ_F [b]	totalΦ_{CL} $\times 10^3$	rel Φ_S ($\Phi_S/\Phi_{S(H)}$)	$\sigma_p{}^{+c}$	HOMO[d] (eV)
3a	Me_2N	0.56	7.22	33.0	−1.7	−7.91
3b	MeO	0.38	2.13	3.60	−0.778	−8.14
3c	H	1.00	0.58	1.00	0	−8.33
3d	CN	0.77	0.069	0.16	0.659	−8.74

[a] [TsQD] = 1.0×10^{-5} M in THF, [Distyrylbenzenes] = 2.0×10^{-4} M in THF, [H_2O_2] = 3.0×10^{-1} M in H_2O. [b] Measured in THF/H_2O. [c] Reference 18. [d] Calculated by PM3.

Alternatively, we used a series of highly fluorescent para,para′-disubstituted distyrylbenzenes (DSBs, **3a**–**d**)[16] as the fluorophores whose electronic effect can be controlled by the substituents while retaining structural equality. Several DSBs have been used as the fluorophores in the TCPO-CL system,[17] but a correlation of the electronic nature of the substituents with the CL efficiency was investigated in this study. The collected data in Table 3 show that the total Φ_{CL} does not depend on the fluorescence quantum yield (Φ_F) of **3** but increases with the electron-donating ability of the substituents. The relative Φ_S, the singlet excitation yield expressed as the quotient Φ_{CL}/rel Φ_F, shows a tendency to increase with



3a, R = Me_2N **3c**, R = H
3b, R = MeO **3d**, R = CN

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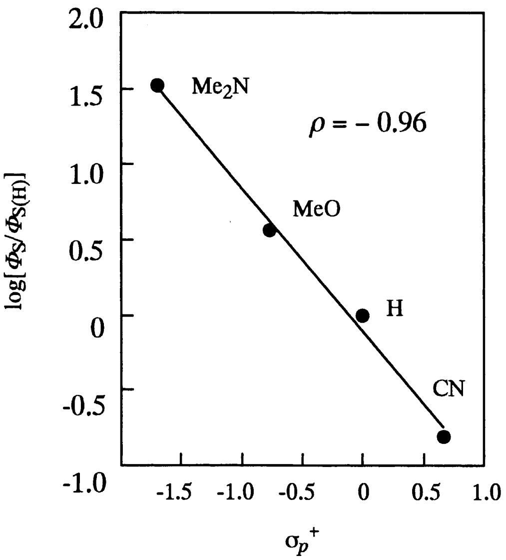

FIGURE 3. Hammett relationship between $\sigma_p{}^+$ and logarithm of relative Φ_S in TsQD-CL in the presence of para,para′-disubstituted distyrylbenzenes.

the fall of the $\sigma_p{}^+$ value as well as with a rise in the HOMO energy. Both the $\sigma_p{}^+$ values[18] and HOMO energies are known to be closely related to oxidation potentials.[19,20] Gollnick et al.[19] documented a linear relationship between the σ^+ values and the oxidation potentials of substituted diarylethenes. Because of the difficulty in measuring oxidation potentials due to poor solubility of DSBs in most organic solvents, σ^+ values were regarded as excellent substitutes for the oxidation potentials. To verify the CIEEL mechanism in the decomposition of organic peroxides, a linear correlation of the logarithm of corrected CL intensities (singlet excitation yields) with the oxidation potential of the fluorophores has sometimes been documented.[21] As shown in Figure 3, the plot of log(rel Φ_S) against the $\sigma_p{}^+$ values showed an excellent Hammett relationship, where the ρ value was −0.98. The negative sign of the ρ value explains that the electron-donating group of the fluorophore promotes the light emission. Additionally, the log(rel Φ_S) is also a linearly increasing function of the HOMO energy of **3**. These results corroborate the contribution of the CIEEL mechanism in the present TsQD-CL. Various DSBs are readily prepared by the Wittig type of reactions; therefore, they are expected to be utilized in the field of CL hereafter.

Experimental Section

General Methods. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ as the solvent, and chemical shifts (δ) were given in ppm relative to tetramethylsilane (TMS) as the internal standard. Mass spectra were determined at an ionizing voltage of 70 eV. Melting points are uncorrected. Solvents and commercially available compounds were purchased from standard suppliers and purified by standard methods. Distyrylbenzenes were prepared by the Horner−Wadsworth−Emmons reaction of 1,4-bis(diethylphosphonomethy)benzene and corresponding aromatic aldehydes according to the literature procedure.[17] The CL quantum yields were measured by a photocounting method using a photomultiplier (R464 Hamamatsu Photonics K.K.) connected with a photocounting unit (C3866), a photocounting board (M3949), and handling software (U3997). The calibration was made by a standard method with luminol chemiluminescence in the presence of tBuOK in dry DMSO (vide infra).

***N*,*N*′-Bistosyl-1*H*,4*H*-quinoxaline-2,3-dione (TsQD).** To a suspension of *N*,*N*′-bistosyl-*o*-phenylenediamine (1.00 g, 2.4 mmol) and oxalyl chloride (0.5 mL, 5.80 mmol) in benzene (160 mL) was added dropwise a solution of triethylamine (1.60 mL, 11.5 mmol) in benzene (10 mL) at room temperature. After the solution was stirred for 3 h, the precipitated triethylamine hydrochloride was removed by filtration. After concentration of the filtrate, the residue was washed with ether to give a crude product (0.88 g, 79%), which was recrystallized from benzene to yield an analytically pure product: mp 196−197 °C; IR (Nujol) 1740 cm^{-1}; ^{1}H NMR δ 2.45 (s, 6H, C*H*$_3$), 7.35 (d, 2H, *J* = 10.1 Hz, *H*-6 and 7), 7.36 (d, 4H, *J* = 8.6 Hz, *o-H* in Ts), 7.82−7.84 (m, 2H, *H*-5 and 8), 8.01 (d, 4H, *J* = 8.6 Hz, *m-H* in Ts); ^{13}C NMR δ 24.0 (*C*H$_3$), 122.1, 124.5, 126.9, 129.7, 130.4, 134.6, 147.1 (aromatic *C*), 153.4 (*C*═O); MS (*m*/*z*) 470 (M$^+$). Anal. Calcd for $C_{22}H_{18}O_6N_2S_2$: C, 56.16; H, 3.86; N, 5.96. Found: C, 56.14; H, 3.80; N, 6.01.

6-Carbethoxy-*N*,*N*′-bistosyl-1*H*,4*H*-quinoxaline-2,3-dione (TsQDEs). This compound was prepared from ethyl (3,4-*N*,*N*′-bistosylamino)benzoate (1.00 g, 2.05 mmol)), oxalyl chloride (0.21 mL, 2.45 mmol), and triethylamine (0.68 mL, 4.89 mmol) in a manner similar to that described above. Recrystallization from ethyl acetate gave a product with 1 mol of ethyl acetate in 48% yield (0.62 g): mp 182−183 °C (as TsQD·AcOEt); IR (Nujol) 1744, 1721 cm^{-1}; ^{1}H NMR (as TsQDEs·AcOEt) δ 1.43 (t, 3H, $CH_3COOCH_2CH_3$, *J* = 7.0 Hz), 2.46 (s, 6H, $SO_2C_6H_4CH_3$), 4.41 (q, 2H, $CH_3COOCH_2CH_3$, *J* = 7.0 Hz), 7.38 (d, 2H, *J* = 8.1 Hz, *o-H* in Ts), 7.40 (d, 2H, *J* = 8.4 Hz, *o-H* in Ts), 7.90 (d, 1H, *J* = 8.8 Hz, *H*-7), 7.97 (dd, 1H, *J* = 8.8 Hz, *H*-8), 8.02 (d, 2H, *J* = 8.3 Hz, *m-H* in Ts), 8.10 (d, 2H, *J* = 8.6 Hz, *m−H* in Ts), 8.47 (d, *J* = 1.8 Hz, *H*-5); ^{13}C NMR δ 14.7 ($CH_3COOCH_2CH_3$), 22.2 ($SO_2C_6CH_4CH_3$), 62.1 (CH_3COOCH_2-CH_3), 121.8, 123.1, 124.5, 127.6, 127.9, 128.8, 129.7, 129.8, 130.5, 130.6, 134.3, 134.6, 147.4, 147.5 (aromatic *C*), 153.0, 153.1 (NTs*C*O), 165.0 ($CH_3COOCH_2CH_3$); MS (*m*/*z*) 514 (M$^+$ − Et). Anal. Calcd for $C_{29}H_{30}O_{10}N_2S_2$ (as TsQD·AcOEt): C, 55.23; H, 4.79; N, 4.44. Found: C, 55.23; H, 4.43; N, 4.51.

Bis(*N*-phenyl-*N*-tosyl)oxamide (1). This compound was prepared in 55% yield (1.82 g) from *N*-phenyltosylamide (3.00 g, 12.15 mmol)), oxalyl chloride (0.53 mL, 6.17 mmol), and triethylamine (1.72 mL, 12.36 mmol) in a manner similar to that described above. Recrystallization from ethyl acetate gave a product with 0.5 mol of ethyl acetate: mp 209−211 °C (with 0.5 mol of AcOEt); IR (Nujol) 1680, 1708 cm^{-1}; ^{1}H NMR δ 2.41 (s, 6H, C*H*$_3$), 7.18−7.43 (m, Ar*H* and *o*-Ar*H* of Ts), 7.72 (d, 4H, J_H = 7.8, *m*-Ar*H* of Ts); ^{13}C NMR δ 24.0 (*C*H$_3$), 129.8, 130.0, 130.4, 130.8, 133.7, 134.4, 146.1 (aromatic *C*), 162.8 (*C*═O); MS (*m*/*z*) 548 (M$^+$). Anal. Calcd for $C_{60}H_{56}N_4O_{14}S_4$ (as oxamide, AcOEt = 2:1): C, 60.79; H, 4.76; N, 4.73. Found: C, 60.74; H, 4.61; N, 4.93.

2,4,6-Trichlorophenyl (*N*-Phenyl-*N*-tosyl)oxamoylformate (2). To a solution of oxalyl chloride (0.78 mL, 9.11 mmol) in benzene (20 mL) were successively added a solution of *N*-phenyl-*N*-tosylamide (1.50 g, 6.70 mmol) in benzene (20 mL) and a solution of triethylamine (0.84 mL, 6.07 mmol) in benzene (25 mL). After the solution was stirred for 30 min at room temperature, triethylamine hydrochloride was removed by filtration. The filtrate was concentrated in vacuo to yield *N*-phenyl-*N*-tosylchlorocarbonylformamide (1.71 g, 83%), which was subjected to the next reaction without purification. To a solution of the thus-prepared crude *N*-phenyl-*N*-*p*-toluenesulfonylchlorocarbonylformamide (1.71 g, 5.06 mmol) in ben-

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zene (20 mL) were successively added a solution of 2,4,6-trichlorophenol (1.00 g, 5.06 mmol) in benzene (20 mL) and a solution of triethylamine (0.7 mL, 5.06 mmol) in benzene (20 mL). After being stirred for 1 h at room temperature, the precipitate of triethylammonium hydrochloride was removed by filtration, and the filtrate was concentrated. The residual product was recrystallized in benzene−hexane to yield the pure product (1.12 g, 37%): mp 168−170 °C; IR (Nujol) 1769, 1709 cm^{-1}; ^{1}H NMR δ 2.47 (s, 3H, C*H*$_3$), 7.28−7.50, 7.88 (m, 11H, aromatic *H*); ^{13}C NMR δ 22.2 (*C*H$_3$), 129.14, 129.77, 130.15, 130.24, 131.22, 133.44, 133.53, 134.50, 141.82, 146.62, (aromatic *C*), 156.49, 156.28 (PhTsN*C*O), 158.49 (*C*OOTCP); MS (*m*/*z*) 350 ($M^+ - PhNCO - CO$), 326 ($M^+ - CH_3C_6H_4SO_3^{\bullet}$). Anal. Calcd for $C_{21}H_{14}NO_5S$: C, 50.57; H, 2.83; N, 2.81. Found: C, 50.31; H, 2.62; N, 2.66.

Calibration of a Photomultiplier. It is known[15] that autoxidation of a luminol solution having an absorbance of 1.0 in the presence of excess *t*-BuOK in *t*-BuOH produces photons of 1.62 × 10^{-6} mol/L; therefore, the correction value (G) for the photomultiplier is defined by the following equation

$$G = (1.62 \times 10^{-6})\mathrm{Abs}_{\mathrm{lumi}} \times V_{\mathrm{lumi}}/N_{\mathrm{lumi}}$$

where $\mathrm{Abs}_{\mathrm{lumi}}$ is the absorbance, V_{lumi} the volume of the luminol solution, and N_{lumi} the count number determined by an average of at least five measurements. Because a luminol solution suitable for the capacity of the photomultiplier used in this study was required, the absorbance at 359.5 nm of a stock luminol solution (1.6 × 10^{-7} M) in distilled DMSO was determined to be 1.22 × 10^{-3} from a calibration curve of the luminol solution. To this luminol solution (2.0 mL) in a quartz cell was added *t*-BuOK solution (0.3 mL, 2.0 × 10^{-2} M) in *t*-BuOH, and the photons generated immediately were counted. The G value was calculated according to the above equation.

Measurement of the CL Quantum Yields. The total CL quantum yields (Φ_{CL}) were calculated according to the equation

$$\Phi_{\mathrm{CL}} = GN(R_{\mathrm{photo}}/M)$$

where N is the average number of the counts, R_{photo} the correction factor given by the manufacturer for the fluorescence emission maximum of the fluorophores, and M the moles of TsQD or other substrates. For a typical run of perylene-enhanced TsQD-CL, a solution (1.5 mL) containing TsQD (1.00 × 10^{-5} M) and perylene (2.00 × 10^{-4} M) in dry THF was placed in a 1 × 1 cm quartz cuvette in front of the photomultiplier in exactly the same geometry. Photocounting was initiated simultaneously with the injection of 0.5 mL of a H_2O_2 solution (3.00 × 10^{-1} M) into the cuvette, and the data collection was continued for 204 s. The total CL quantum yields were calculated according to the above equation.

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