Synthesis of 4-Styrylphthalhydrazides and Their Chemiluminescence Reaction. Emitters and Chemiluminescence Efficiency Highly Dependent on Electronic Nature of Styryl Goups

Jiro Motoyoshiya,* Kazuya Yokota, Takuro Fukami, Shoji Konno, Aya Yamamoto,
Masanori Hotta, Ryu Koike, Sachiko Yoshioka, Yoshinori Nishi, and Hiromu Aoyama

Department of Chemistry, Faculty of Textile Science and Technology, Shinshu University,
Ueda, Nagano, 386-8567, Japan

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A series of 4-styrylphthalhydrazides were synthesized and their chemiluminescence reactions were investigated. The chemiluminescence quantum yields as well as the emitters were variable depending on the electronic nature of the terminal substituents attached on the styryl groups. It was revealed that the excited phthalate ions were the emitters when they were highly fluorescent, while the energy transfer chemiluminescence from the excited phthalate ions to the phthalhydrazide anions took place when the fluorescence of the corresponding phthalate ions were very weakly fluorescent.

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Of the artificial chemiluminescent compounds, luminol (5-amino-2,3-dihydro-1,4-phthalazinedione, **1**) (Figure 1) is the most popular one [1], which has been used in practical applications as a means of chemical analysis [2]. The luminol chemiluminescence is based on light emission from the excited 3-aminophthalate ion (**2**) generated by oxidation with hydrogen peroxide or atmospheric oxygen in the presence of bases and catalysts [3]. This peculiar chemiluminescence property and its practical value have attracted continuous interest and prompted many chemists to investigate its reaction in detail [4] and to exploit related chemiluminescent compounds to date [5]. For instance, several modified phthalhydrazides, some of which display chemiluminescence stronger than luminol, have been synthesized [3a,6]. In contrast, phthalhydrazide (**3**), structurally the parent compound of luminol but lacking the amino group, also weakly emits light by oxidation, in which the emitter is not a non-fluorescent phthalate ion, but the excited phthalhydrazide monoanion generated by energy transfer from the excited phthalate ion as reported by White *et. al* [7]. They also reported a very unique reaction, photochemistry without light, of 4-styrylphthalhydrazide (**4a**), in which the *cis-trans* isomerization occurred with a low efficiency [8]. Such diversity in the phthalhydrazide chemiluminescence encouraged us to synthesize various 4-styrylphthalhydrazides and investigate their chemiluminescence reaction with expectation of finding new aspects.

As illustrated in Scheme 1, a series of dimethyl 4-styrylphthalates, prepared by the Horner-Wadsworth-Emmons reaction of dimethyl (4-dimethylphosphonomethyl)phthalate and various aromatic aldehydes, were reacted with hydrazine to give 4-styrylphthalhydrazides (**4a-g**). With an expectation of increasing the chemiluminescence efficiency due to an increase of the fluorescence intensity of the phthalate ion by the prolonged conjugation [9], **4g** having a distyrylbenzene moiety was designed.

The fluorescence intensity of the 4-styrylphthalate ions, the most likely emitters in the phthalhydrazide chemiluminescence, is strongly dependent on the electronic nature of the terminal substituents (Table 1). The phthalates with electron-donating substituents exhibit fluorescence in a longer wavelength region, in addition to the higher Φ_F, than those without such substituents. This phenomenon is due to an increase in push-pull character for the conjugated system. Therefore, chemiluminescence property is also expected to vary with the terminal substituents.

The reactions of the 4-styrylphthalhydrazides (**4a-g**) in the aerobic DMSO solution in the presence of *tert*-BuOK provided chemiluminescence with various intensities depending on the structures. These chemiluminescence reactions produced the corresponding phthalate ions as the final products that were identified by their UV spectra. The 4-styrylphthalhydrazides **4a** and **4b** showed a very weak light emission with a much longer wavelength around 530 nm than was expected from the corresponding phthalate

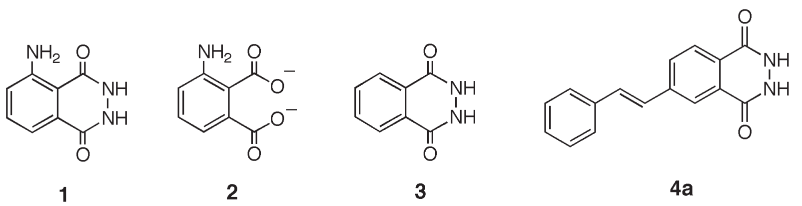
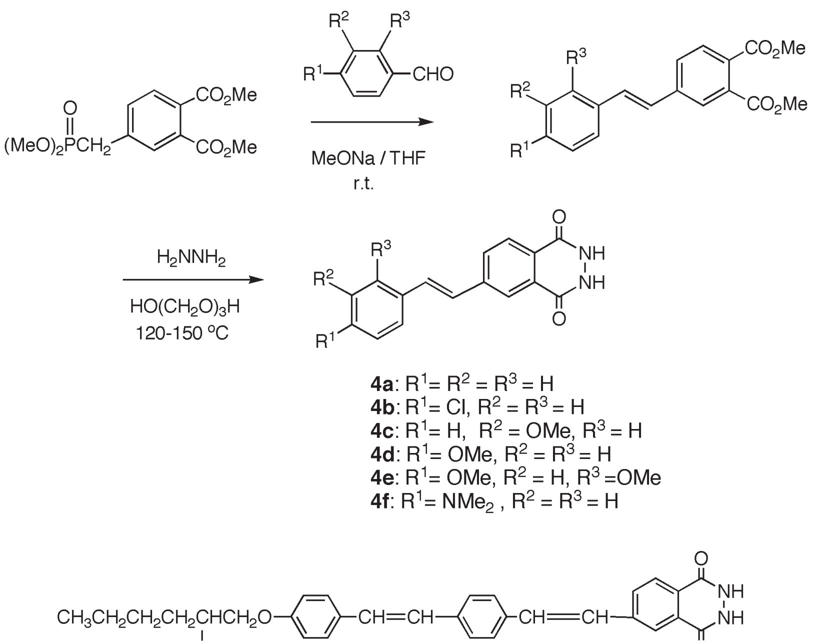


Figure 1

Scheme 1

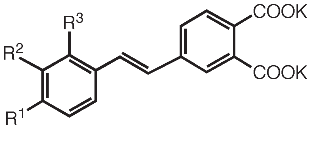
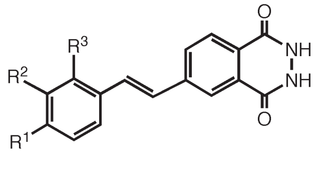
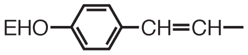


4a: R^1= R^2 = R^3 = H
4b: R^1= Cl, R^2 = R^3 = H
4c: R^1= H, R^2 = OMe, R^3 = H
4d: R^1= OMe, R^2 = R^3 = H
4e: R^1= OMe, R^2 = H, R^3 =OMe
4f: R^1= NMe$_2$, R^2 = R^3 = H

4g

Table 1

Fluorescence Spectral Data of the Dipotassium Phthalates and Chemiluminescence Quantum Yields (rel.Φ_{CL}) of the Reactions of Phthalhydrazides (**4e-g**)

			
Substituent	Fluorescence of the potassium phthalates		Chemiluminescence quantum yield of **4**
	λ_{max} [a]	Φ_F [b]	Φ_{CL} x 10^2 [c]
R^1= R^2 = R^3 = H	363	0.025	[d]
R^1= Cl, R^2 = R^3 = H	370	0.038	[d]
R^1= H, R^2 = OMe, R^3 = H	368	0.036	[d]
R^1= OMe, R^2 = R^3 = H	377	0.071	[d]
R^1= OMe, R^2 = H, R^3 =OMe	397	0.096	0.12
R^1= NMe$_2$, R^2 = R^3 = H	452	0.16	0.2
R^1=  EHO CH=CH R^2 = R^3 = H EH = CH$_3$(CH$_2$)$_3$CH(CH$_2$CH$_3$)CH$_2$	442	0.30	2.3

[a] Measured in DMSO in the presence of ^{t}BuOK: fluorescence was recorded by irradiation at the absorption maximum; [b] Determined by comparison with 9,10-diphenylanthracene; [c] Determined by comparing with luminol chemiluminescence: photons were counted during 512 sec after the reactions were started; [d] Could not be determined because of dual emission with the different wavelengths.

ions. As shown in Figure 2, the chemiluminescence spectrum of **4a** was different from the fluorescence spectrum of the corresponding phthalate ion but agreed with the fluorescence spectrum (emission at λmax. 530 nm) measured immediately after **4a** and *tert*-BuOK were mixed in DMSO. The resulting solution after a few hours showed only the fluorescence corresponding to the phthalate ion (emission at λmax. 363 nm). Figure 3 shows the time course of the fluorescence spectra for the reaction of **4a**. The fluorescence at 530 nm formed initially almost maintained its intensity during several ten minutes with a bit of decay, while that of the phthalate ion at 363 nm increased constantly. Considering the similarity of the present chemiluminescence reaction and that of the parent phthalhydrazide (**3**) [8], in which the phthalhydrazide monoanion exhibited the fluorescence at 526 nm and was stable toward oxygen, the fluorescence at 530 nm observed here would be ascribed to the monoanion of **4a** that is in an equilibrium state with its dianion finally oxidized to the phthalate ion as shown in Scheme 2. Because of the very weakly fluorescent property of the phthalate ions (**7**) in the case for **4a** and **4b**, the more fluorescent, excited monoanion (**5**) would be produced by an energy transfer from the excited phthalate ions (**7***). Such an energy transfer chemiluminescence was also reported in the reaction of luminol [10], in which a strongly fluorescent dye such as fluores-

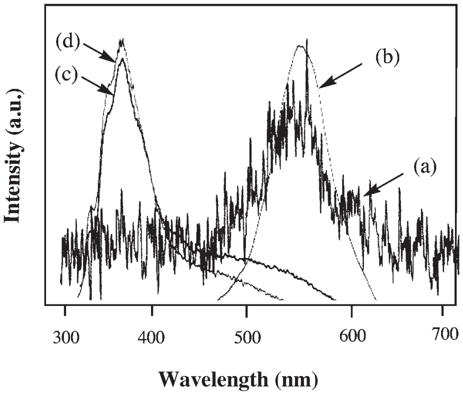


Figure 2. Fluorescence and chemiluminescence spectra of **4a** in DMSO in the presence of ^{t}BuOK. (a) chemiluminescence spectrum, (b) fluorescence at the beginning of the reaction, (c) fluorescence of the potassium phthalate, (d) fluorescence of the resulting solution.

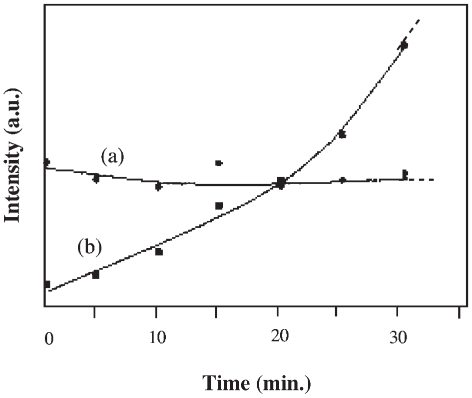
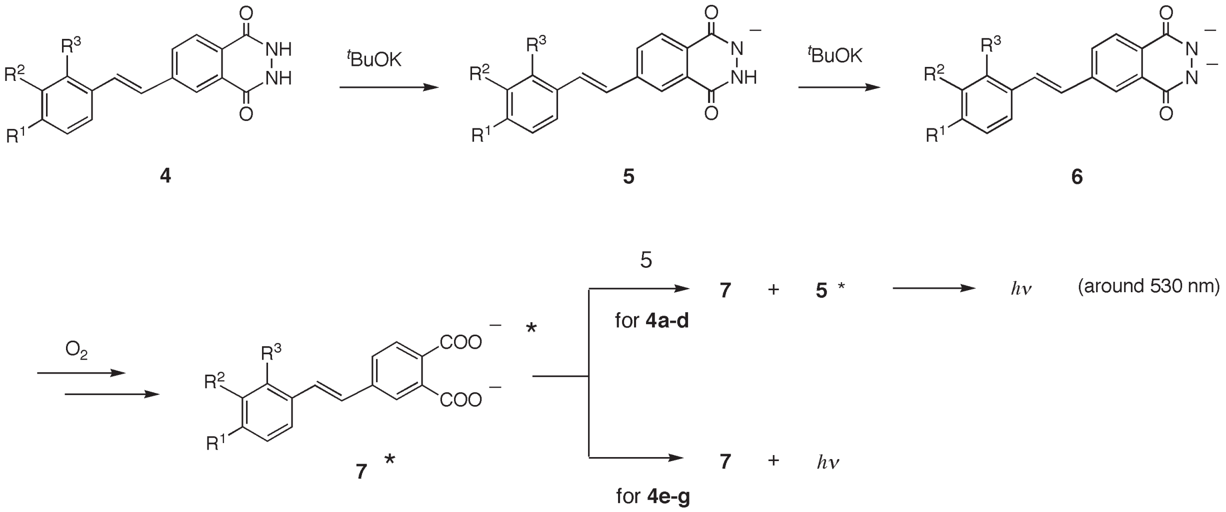


Figure 3. Time course of the fluorescence in the reaction of **4a**. Monitoring at 363 nm (a) and at 536 nm (b).

Scheme 2



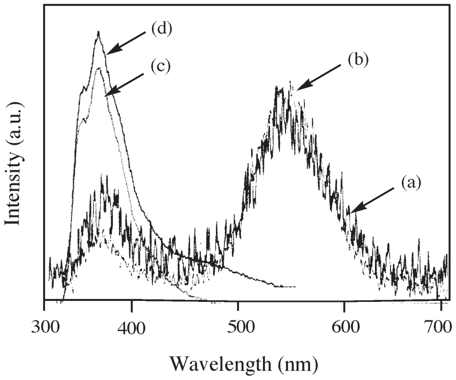


Figure 4. Fluorescence and chemiluminescence spectra of **4c** in DMSO in the presence of ^{t}BuOK. (a) chemiluminescence spectrum, (b) fluorescence at the beginning of the reaction (overlapping), (c) fluorescence of the potassium phthalate, (d) fluorescence of the resulting solution.

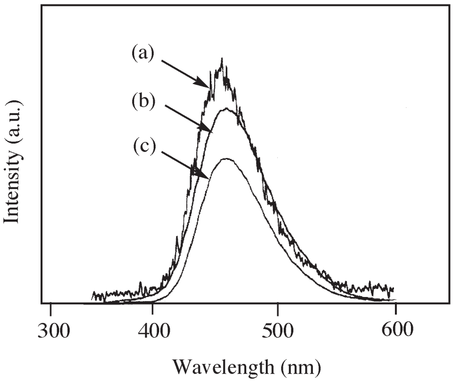


Figure 5. Fluorescence and chemiluminescence spectra. (a) Chemiluminescence for **4d**, (b) Resulting solution of **4d**, (c) Fluorescence for dipotassium 4-(4'-dimethylamino-styryl)phthalate, (d) Fluorescence for **4d**.

cein was an energy acceptor. As expected, a bright yellow chemiluminescence was also observed when fluorescein was used as an energy acceptor in the reaction of **4a** or **4b**.

In the reactions of **4c** and **4d**, the dual light emission around 370 nm and 530 nm, ascribed to the phthalate ions and the phthalhydrazide monoanions, respectively, could be detected as shown in Figure 4. In these cases, both direct and indirect (energy transfer) chemiluminescence reactions are involved owing to an increase of fluorescence character of the phthalate ions compared to the case of **4a** and **4b**.

On the contrary, **4e-g** bearing the strongly electron-donating substituents produced the chemiluminescence only based on the fluorescence of the corresponding potassium phthalates, whose chemiluminescence quantum yields (Φ_{CL}) were comparable to the luminol chemiluminescence (Table 1). Figure 5 shows a good agreement of the fluorescence and chemiluminescence spectra of the reaction of **4f**. Especially, **4g** showed the most effective chemiluminescence by *ca.* 4 times larger than luminol. The fast decay of the anions of the phthalhydrazides **4e-g** revealed by monitoring of their absorptions suggests that their anions are easily oxidized to the phthalate ions. Since the phthalhydrazide chemiluminescence reaction is believed to involve a superoxide anion formed by an electron transfer from the phthalhydrazide dianion to molecular oxygen at the initial stage [4f], the electron-donating substituent would promote an electron transfer from the hydrazide dianion to a molecular oxygen and the sequential oxidation process, resulting in the fast formation of the excited phthalate ions. In addition, a photoisomerization from *E*-**4f** to *Z*-**4f** was detected in *ca.* 3% yield during this chemiluminescence reaction similarly to the reaction of **4a** as reported by White *et al.* [8].

The chemiluminescence reaction in an aqueous medium was also examined employing **4f**. In contrast to the reaction under the anhydrous conditions, the emission efficiency of **4f** was inferior to luminol by one tenth and the emission red-shifted by *ca.* 50 nm [11] when the reaction was carried out in an aqueous DMSO solution using potassium persulfate and potassium carbonate as the oxidizing agent and base.

In summary, a series of 4-styrylphthalhydrazides were prepared and their chemiluminescence reactions were examined, where modulation of the chemiluminescence efficiency as well as the emitter by the electronic nature of the terminal substituents was conducted. The strongly electron-donating character is coincident with the increase in the Φ_F of the corresponding phthalate ions by a contribution of an electronic push-pull system, which provides an efficient chemiluminescence with the excited phthalate ions being the emitters. On the other hand, the energy transfer chemiluminescence takes place when Φ_F of the phthalate ions is small.

EXPERIMENTAL

The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz, 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. All phthalhydrazides did not melt bellow 260 °C. The CL quantum yields were measured by the procedure previously reported [12].

General Procedure for Synthesis of 4-Styrylphthalhydradide (**4a**) [8].

The Arbuzov reaction of trimethyl phosphite (2.83 mL, 24.0 mmol) and dimethyl 4-bromomethylphthalate (6.89 g, 24.0 mmol) was carried out by heating their mixture for 18 h at 120 °C. The residue was purified by column chromatography on silica gel to give the pure phosphonate (3.95 g, 52 %), a part of which (1.0 g, 3.16 mmol) was subjected to the Horner-Wadsworth-Emmons reaction with benzaldehyde (0.26 mL, 2.53 mmol) in the presence of *tert*-BuOK (0.43 g, 3.79 mmol) in THF (6 mL) for 15 h at room temperature with stirring. After removal of the solvent, benzene was added and the organic layer was washed with saturated ammonium chloride. Standard workup consisting of drying over Na_2SO_4, concentration under reduced pressure, and recrystallization gave dimethyl 4-styrylphthalate (0.49 g, 65%). Thus prepared dimethyl 4-styrylphthalate ester (0.3 g, 1.01 mmol) was dissolved in warm triethylenglycol (5 ml), and distilled hydrazine (1.62 mL, 50.6 mmol) was added to the solution. After heating for 1 h at 100 °C, hexane was added until the 4-styrylphthalhydrazide was precipitated and the excess reactants were removed *in vacuo* at 100 °C to give a yellow powder (0.077 g, 29 %), ir: NH 3302, CO 1605 cm^{-1}; ^1H nmr: (DMSO-d_6): δ 6.30 (br, 2H, NH), 7.32 (t, 1H, 4”-H, *J* = 7.6 Hz), 7.42 (t, 2H, 3', 5'-H, *J* = 7.6 Hz), 7.47 (d, 1H, PhCH=C*H*, *J* = 16.5 Hz), 7.52 (d, 1H, PhCH=C*H*, *J* = 7.69 Hz), 7.69 (d, 2H, 2', 6'-H, *J* = 7.6 Hz), 8.06 (d, 1H, 5-H, *J* = 7.6 H), 8.09 (d, 1H, 6-H, *J* = 7.6 Hz), 8.24 (s, 1H, 3-H); ^{13}C NMR (DMSO-d_6): δ 123.54, 126.20, 127.27, 127.32, 127.69, 128.59, 128.78, 129.12, 129.75, 131.65, 136.96, 140.89, 156.01, 156.35; hrms (EI): calcd for $C_{16}H_{12}N_2O_2$ (M^+) 264.0898, found 264.0907.

4-(4'-Chlorostyryl)phthalhydrazide (**4b**).

This compound was obtained as a pale-yellow powder in 46% yield, ir: NH 3178, CO 1655 cm^{-1}; ^1H nmr (DMSO-d_6): δ 5.70 (br, 2H, NH), 7.47 (d, 2H, 2', 6'-H *J* = 8.4 Hz), 7.51 (s, 2H, C*H*=C*H*), 7.72 (d, 2H, 3', 5'-H, *J* = 8.4 Hz), 8.07 (d, 1H, 5-H, *J* = 8.4 Hz), 8.09 (d, 1H, 6-H, *J* = 8.4 Hz), 8.24 (s, 1H, 3-H); ^{13}C nmr (DMSO-d_6): δ 123.63, 126.16, 127.17, 128.48, 128.93, 129.13, 129.80, 129.96, 130.43, 132.95, 135.95, 140.79, 155.61, 156.02; ms: *m/z* 298 (M^+).

Anal. Calcd. for $C_{16}H_{11}ClN_2O_2$: C, 64.33; H, 3.71; N, 9.38. Found: C, 64.47; H, 3.76; N, 9.45.

4-(3'-Methoxystyryl)phthalhydrazide (**4c**).

This compound was obtained as a pale-yellow powder in 46 % yield, ir: NH 3198, 3310, CO 1658 cm^{-1}; ^1H nmr (DMSO-d_6): δ 3.82 (s, 3H, OCH_3), 6.50 (br, 2H, NH), 6.89 (d, 1H, 6'-H, *J* = 7.6 Hz), 7.25 (d, 1H, 4'-H, *J* = 7.6 Hz), 7.28 (s, 1H, 2'-H), 7.32 (dt, 1H, 5'-H, *J* = 7.6 Hz), 7.44 (d, 1H, $CH_3OC_6H_4CH=C\mathit{H}$, *J* = 16.6 Hz), 7.52 (d, 1H, $CH_3OC_6H_4C\mathit{H}=CH$, *J* = 16.6 Hz), 8.06 (s, 2H, 5, 6-H), 8.24 (s, 1H, 3-H); ^{13}C nmr (DMSO-d_6): δ 55.45, 112.21, 114.51, 119.87, 123.64, 126.22, 127.46, 128.03, 129.23, 129.65, 130.10, 131.49, 138.44, 140.75, 156.19, 156.51, 159.97; ms: *m/z* 294 (M^+).

Anal. Calcd. For $C_{17}H_{14}N_2O_3$: C, 69.38; H, 4.79; N, 9.52. Found: C, 69.28; H, 4.95; N, 9.46.

4-(4'-Methoxystyryl)phthalhydrazide (**4d**).

This compound was obtained as a pale-yellow powder in 79% yield, ir: NH 3340, CO 1600 cm^{-1}; ^1H nmr (DMSO-d_6): δ 3.80 (s, 3H), 6.30 (br, 2H, NH), 6.98 (d, 2H, 1', 5'-H, *J* = 8.8 Hz), 7.32 (d, 1H, $CH_3OC_6H_4CH=C\mathit{H}$, *J* = 16.4 Hz), 7.46 (d, 1H, $CH_3OC_6H_4C\mathit{H}=CH$, *J* = 16.4 Hz), 7.64 (d, 2H, 2', 4'-H, *J* = 8.8 Hz), 8.02 (d, 1H, 5-H, *J* = 8.0 Hz), 8.04 (d, 1H, 6-H, *J* = 8.0 Hz), 8.18 (s, 1H, 3-H); ^{13}C (DMSO-d_6): δ 55.56, 114.62, 122.95, 125.26, 126.08, 126.62, 128.71, 128.85, 129.58, 129.64, 131.50, 141.50, 155.68, 155.98, 159.86; ms: *m/z* 294 (M^+).

Anal. Calcd. For $C_{17}H_{14}N_2O_3$: C, 69.38; H, 4.79; N, 9.52. Found: C, 69.38; H, 4.67; N, 9.69.

4-(2',4'-Dimethoxystyryl)phthalhydrazide (**4e**).

This compound was obtained as a pale-yellow powder in 41 % yield, ir: NH 3256, CO 1608 cm^{-1}; ^1H nmr (DMSO-d_6): δ_3.81 (s, 3H, CH_3O), 3.89 (s, 3H, CH_3O), 6.58-6.62 (m, 2H, 2', 5'-H), 6.70 (br, 2H, NH), 7.31 (d, 1H, $(CH_3O)_2C_6H_3CH=C\mathit{H}$, *J* = 16.6 Hz), 7.55 (d, 1H, $(CH_3O)_2C_6H_3C\mathit{H}=CH$, *J* = 16.6 Hz), 7.66 (d, 1H, 4'-H, *J* = 8.8 Hz), 7.96 (d, 1H, 5-H, *J* = 8.4 Hz), 8.03 (d, 1H, 6-H, *J* = 8.4 Hz), 8.14 (s, 1H, 3-H); ^{13}C nmr (DMSO-d_6): δ 55.68, 55.98, 98.73, 106.19, 118.14, 122.65, 125.59, 125.91, 126.28, 127.00, 128.16, 129.27, 129.37, 141.61, 156.32, 156.62, 158.46, 161.25; ms: *m/z* 324 (M^+).

Anal. Calcd. For $C_{18}H_{16}N_2O_4$: C, 66.66; H, 4.97; N, 8.64. Found: C, 66.54; H, 5.04; N, 8.85.

4-(4'-Dimethylaminostyryl)phthalhydrazide (**4f**).

This compound was obtained as a yellow powder in 59 % yield, ir: NH 3190, CO 1600 cm^{-1}; ^1H nmr (DMSO-d_6): δ 2.95 (s, 6H. $(CH_3)_2N$), 6.30 (br, 2H, NH), 6.74 (d, 2H, 2', 5'-H, *J* = 8.8 Hz), 7.14 (d, 1H, $(CH_3)_2NC_6H_4CH=C\mathit{H}$, *J* = 16.4 Hz), 7.38 (d, 1H, $(CH_3)_2NC_6H_4C\mathit{H}=CH$, *J* = 16.4 Hz), 7.51 (d, 2H, 3', 4'-H, *J* = 8.8 Hz), 8.01 (s, 2H, 5,6-H), 8.13 (s, 1H, 3-H); ^{13}C nmr (DMSO-d_6): δ 40.23, 112.48, 122.36, 122.51, 124.68, 126.04, 126.14, 128.49, 128.86, 129.35, 132.26, 142.08, 150.76, 155.80, 156.01; ms: *m/z* 307 (M^+).

Anal. Calcd. For $C_{18}H_{17}N_3O_2$: C, 70.34; H, 5.58; N, 13.67. Found: C, 70.73; H, 5.43; N, 13.99.

4-{4'-[4"-(2-Ethylhexyloxy)styryl]styryl}phthalhydrazide (**4g**).

This compound was obtained as a yellow powder in 54 % yield, ir: NH 3192, CO 1593, 1654 cm^{-1}; ^1H nmr (DMSO-d_6): δ 0.88-1.71 (m, 15H, $C_7\mathit{H}_{15}$ CH_2O, 15H), 3.89 (d, 2H, C_7H_{15} $C\mathit{H}_2O$, *J* = 6.0 Hz), 6.96 (d, 2H, 2"", 6""-H, *J* = 8.8 Hz), 7.11 (d, 1H, C_7H_{15} $CH_2OC_6H_4CH=C\mathit{H}$, *J* = 16.4 Hz), 7.26 (d, 1H, C_7H_{15} $CH_2OC_6H_4C\mathit{H}=CH$, *J* = 16.4 Hz), 7.50 (d, 2H, $CH=C\mathit{H}C_6H_3$-$(CONH)_2$, *J* = 16.4 Hz), 7.51 (d, 2H, $C\mathit{H}=CHC_6H_3(CONH)_2$, *J* = 16.4 Hz), 7.55 (d, 2H, 3", 5"-H, *J* = 8.8 Hz), 7.61 (d, 2H, 2", 6'-H, *J* = 8.2 Hz), 7.69 (d, 2H, 3', 5'-H, *J* = 8.2 Hz), 8.05 (d, 1H, 5-H, *J* = 8.0 Hz), 8.15 (d, 1H, 6-H, *J* = 8.0 Hz), 8.22 (s, 1H, 3-H); ^{13}C nmr ($CDCl_3$), δ (ppm): 11.12, 14.08, 23.06, 23.89, 29.10, 30.55, 39.41, 52.55, 52.72, 70.65, 114.82, 125.75, 125.97, 126.64, 127.23, 127.79, 128.16, 128.37, 128.88, 129.35, 129.72, 129.80, 131.67, 133.40, 135.25, 138.07, 140.84, 159.38, 167.39, 168.53; ms: *m/z* 494 (M^+). The elemental analysis did not give the correct values.

Measurements of the Chemiluminescence Quantum Yields.

Calibration of a photomultiplier was done by the procedure previously reported [12]. For a typical run, a solution (1.0 mL) containing **4** (1.00 x 10^{-5} *M*) in distilled DMSO was placed in a 1 x 1 cm quartz cuvette in front of the photomultiplier in exactly the same geometry. Photon-counting was initiated simultaneously with the injection of a solution (1.0 mL) of *tert*-BuOK (2.00 x 10^{-2} *M*) in DMSO into the cuvette, and the data collection was continued for 2 h.

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