

Chemiluminescent Properties of Fluorene- and Carbazole-Containing Polymeric Fluorophores

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Received February 10, 2000

Fluorene- and carbazole-containing distyrylarylene model and polymeric fluorophores were prepared by reacting 2,7-dibromo-9-butylfluorene and 3,6-dibromo-9-butylcarbazole with styrene and divinylbenzene using the Heck reaction for the chemiluminescence. The UV-vis absorbance, photoluminescence (PL) as well as the chemiluminescence (CL) characteristics of the model and polymeric fluorophores were measured. Sodium salicylate-catalyzed reaction of bis(2,4,6-trichlorophenyl)oxalate (TCPO) with hydrogen peroxide produced a strong chemiluminescent blue light emission with 439-489 nm in the presence of the fluorophore. The wavelength of CL light was similar to that of photoluminescence. The chemiluminescent intensity was decayed according to the exponential equation. The glow of CL maintained more than 12 hr and was visible with naked eye.

Introduction

A major recent development in the field of chemiluminescence (CL) has been caused by the discovery of chemical lighting from the reaction of oxalate esters with hydrogen peroxide and fluorophores.¹⁻¹⁰ Recent advances in CL have created a need for new fluorophores possessing the requisite optical properties. Conventional chemiluminescent fluorophores were highly conjugated aromatic compounds such as perylene, rubrene, 9,10-diphenylanthracene and 9,10-bis(phenylethynyl)anthracene derivatives.¹¹ A particular class of fluorophores of interest is the π -conjugated polymers, which are generally more tractable, stable and less toxic than conventional organic fluorophores.^{12,13}

A method for the chemiluminescence involves intermolecular chemical energy transfer to a fluorescent compound. In the case of polymeric fluorophores, the organized assembly such as micelle maintained a close spacing between 1,2-dioxetanedione and the fluorescent moieties.¹⁴ No examples appeared in the literature applying the polymeric fluorophores to chemiluminescent reaction through energy-transfer processes.

In this article, fluorene- and carbazole-containing distyrylarylene model and polymeric fluorophores were prepared and their CL characteristics including various optical properties were examined.

Experimental Section

Chemicals and Instruments. 2,7-Dibromo-9-butylfluorene and 3,6-dibromo-9-butylcarbazole were prepared by the modified method previously reported.¹⁴⁻¹⁷ Styrene and divinylbenzene (Aldrich Chem. Co.) were purified by vacuum distillation under reduced pressure after drying over calcium hydride. Palladium (II) acetate, tri-*o*-tolylphosphine, tri-*n*-butylamine and bromobenzene (Aldrich Chem. Co.) were

used as received. Bis(2,4,6-trichlorophenyl)oxalate (TCPO) was prepared by the method described previously.¹⁸ Sodium salicylate, pinacol, dibutylphthalate (GR, Yakuri Co.), dimethylphthalate (GR, Junsei Chem. Co.) were used without further purification. Hydrogen peroxide (35%) was concentrated by using anhydrous magnesium sulfate prior to use. All melting points were determined on a melting point apparatus (Aldrich Mel-Temp II) using capillary tubes and were uncorrected. FT-IR spectra were obtained with a Midac Model M-1200 spectrophotometer and ¹H NMR spectra were recorded on a Varian Gemini-2000 spectrometer. Elemental analyses were performed using a Yanaco MT-3 CHN instrument. UV spectra were obtained on a Shimadzu model UV-2100S. Intensity of the emission light was measured with a Minolta Chromameter CS-100. Photoluminescence were measured on an Optical Spectra Multichannel Analyzer (OSMA-1000, Photodiodes 1024).

Representative Preparation of Model Compounds. In a round-bottomed flask (100 mL), were placed 2,7-dibromo-9-butylfluorene (7.9 mmol), styrene (24 mmol) and palladium (II) acetate (0.079 mmol). Tri-*o*-tolylphosphine (1.6 mmol) and tri-*n*-butylamine (1.46 mol) in *N,N*-dimethylformamide (50 mL) were added and the reaction mixture was raised to 100 °C and maintained for 17 hr. The reaction mixture was then cooled and quenched with hydrochloric acid (0.1 N, 5 mL). The powdery product was recrystallized in hexane/toluene (1/1). The reaction of 3,6-dibromo-9-butylcarbazole with styrene was carried out by the similar method described above.

2,7-Distyryl-9-butylfluorene (1): Yield 78%. mp 224-225 °C (uncorrected). IR (KBr): 3070-3020 (s, aromatic C-H), 2950-2870 (s, aliphatic C-H), 1650 (s, C=C), 960, 900 (w, =C-H) cm⁻¹. ¹H NMR (CDCl₃): δ = 7.05-7.75 (m, 20H, aromatic and vinyl protons), 4.02 (t, 1H, methine proton), 2.20 (m, 2H, -CH₂-CH₂-CH₂-CH₃), 1.21 (m, 4H, -CH₂-CH₂-CH₂-CH₃), 0.91 (t, 2H, -CH₂-CH₂-CH₂-CH₃). Anal. Calcd

for C₃₃H₃₀ (426); C, 92.96; H, 7.04. Found: C, 92.81; H, 7.02.

3,6-Distyryl-9-butylcarbazole (2): Yield 82%. mp 231 °C (uncorrected). IR (KBr): 3070-3040 (aromatic C-H), 2950-2870 (aliphatic C-H), 1650 (C=C), 1110-1220 (C-N) cm⁻¹. ¹H NMR (CDCl₃): δ = 8.20-7.02 (m, 20H, aromatic and vinyl protons), 4.43 (t, 2H, =N-CH₂-), 1.92 (m, 2H, -CH₂-CH₂-CH₂-CH₃), 1.42 (m, 2H, -CH₂-CH₂-CH₂-CH₃), 0.98 (t, 3H, -CH₂-CH₂-CH₂-CH₃). Anal. Calcd for C₃₂H₂₉N₁ (427): C, 89.93; H, 6.79; N, 3.29. Found: C, 89.89; H, 6.72; N, 3.31.

Preparation of Copolymers Containing Fluorene and Carbazole Moiety. In a round bottomed flask (100 mL), were placed 2,7-dibromo-9-butylfluorene (7.9 mmol), divinylbenzene (7.9 mmol) and palladium (II) acetate (0.079 mol). Trl-*o*-tolylphosphine (1.6 mmol) in *N,N*-dimethylformamide (50 mL) and trl-*n*-butylamine (1.46 mol) were added and the reaction mixture was raised to 100 °C and maintained for 17 hr. After bromobenzene was added, the reaction mixture was then cooled and quenched with hydrochloric acid (0.1 N, 5 mL). The reaction mixture was precipitated into methanol and powdery product was filtered. The reaction of 3,6-dibromo-9-butylcarbazole with divinylbenzene was carried out by the similar method described above.

3: Yield 85%. IR (KBr): 3050-3020 (aromatic C-H), 2850-2870 (aliphatic C-H), 1640 (C=C), 960, 900 (=C-H) cm⁻¹. ¹H NMR (CDCl₃): δ = 7.7-7.05 (m, 20H, aromatic and vinyl protons), 4.00 (t, 1H, methine protons), 1.92 (m, 2H, -CH₂-CH₂-CH₂-CH₃), 1.00-1.41 (m, 4H, -CH₂-CH₂-CH₂-CH₃), 0.92 (m, 2H, -CH₂-CH₂-CH₂-CH₃). Anal. Calcd for C₂₈H₂₅ (361)_n: C, 93.07; H, 6.93. Found: C, 93.01; H, 6.71.

4: Yield 86%. IR (KBr): 3070-3040 (aromatic C-H), 2950-2870 (aliphatic C-H), 1650 (C=C), 1110-1220 (C-N) cm⁻¹. ¹H NMR (CDCl₃): δ = 8.20-7.02 (m, 20H, aromatic and vinyl protons), 4.43 (t, 2H, =N-CH₂-), 1.93 (m, 2H, -CH₂-CH₂-CH₂-CH₃), 1.41 (m, 2H, -CH₂-CH₂-CH₂-CH₃), 0.97 (t, 3H, -CH₂-CH₂-CH₂-CH₃). Anal. Calcd for C₂₇H₂₄N₁ (362)_n: C, 89.50; H, 6.63; N, 3.87. Found: C, 89.38; H, 6.64; N, 3.85.

Preparation of Chemiluminescent Solution. Model fluorophore (0.3 wt%) and bis(2,4,6-trichlorophenyl)oxalate (TCPO, 20 mmol) was dissolved in dibutylphthalate (200 mL) at 80 °C under nitrogen. On the other hand, hydrogen peroxide (75%, 1.5 equivalent of TCPO) and sodium salicylate (0.25 mmol) were dissolved in 20 mL of mixed solvent of dimethylphthalate/pinacol (3/2). The chemiluminescence was measured by mixing fluorophore solution (0.3 mL) and hydrogen peroxide solution (0.1 mL).

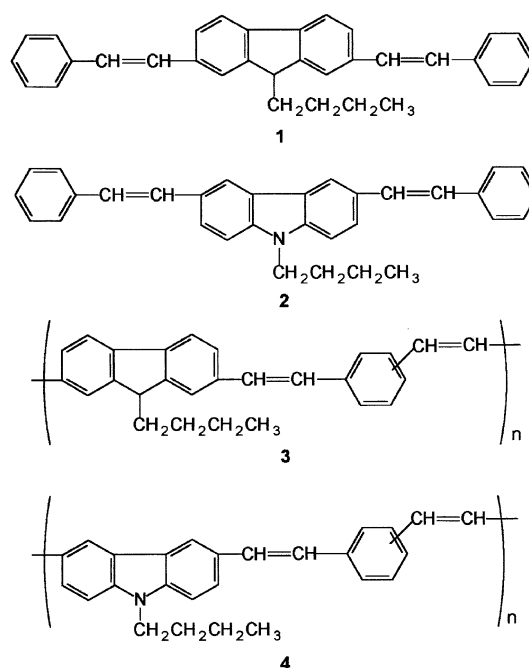
Measurements of Chemiluminescence. Rates of catalytic decomposition of TCPO were determined by monitoring the decay intensity of CL of fluorophore solutions. A cylindrical polyethylene tube (ID, 3 mm; L, 35 mm) was filled with hydrogen peroxide solution (0.1 mL) and glass capillary containing fluorophore solution (0.3 mL) and sealed with a melted PE. The sample was bent to break and placed in the thermostatic sample block of the CL-measuring luminometer. Measurement of the signal was begun by opening the shutter. The chemiluminescent decay was generally recorded for at least 12 hr. Calculation of the rate constant from the intensity vs. time data was performed by a

computer program utilizing a standard least-square treatment. The coefficient was varied less than 5% between replicated sample.

Results and Discussion

Preparation and Characterization of the Model and Polymeric Fluorophores. Fluorene-containing model compound 2,7-distyryl-9-butylfluorene (**1**) was prepared by reacting 2,7-dibromo-9-butylfluorene with styrene in the presence of palladium (II) acetate using the Heck reaction.^{15,16} Also, 3,6-distyryl-9-butylcarbazole (**2**) was synthesized by the reaction of 3,6-dibromo-9-butylcarbazole with styrene. Polymeric fluorophores **3** and **4** containing the same repeating unit were also prepared by reacting 2,7-dibromo-9-butylfluorene and 3,6-dibromo-9-butylcarbazole with divinylbenzene. The synthetic route to model compounds and polymers were well-known in the literature,¹⁵⁻¹⁷ therefore we could obtain all of the fluorophores in high yield. Scheme 1 and Table 1 summarize the results of the preparation of model and polymeric fluorophores. The fluorophores were characterized through the data from proton NMR, IR and elemental analysis. The CHN analysis values agree well with that calculated from the expected chemical structure. The weight average molecular weight (M_w) of **3** and **4** were 5100 and 7200 with a molecular weight distribution of 1.6 and 1.7, respectively. Both polymers were soluble in common organic solvents such as chloroform, tetrahydrofuran and dibutylphthalate.

Optical Properties. The UV absorbance, photoluminescence as well as the CL characteristics of the model and polymeric fluorophores were measured and listed in Table 2. The UV-visible absorption spectra of fluorene containing fluorophores **1** and **3** are shown in Figure 1. The characteris-

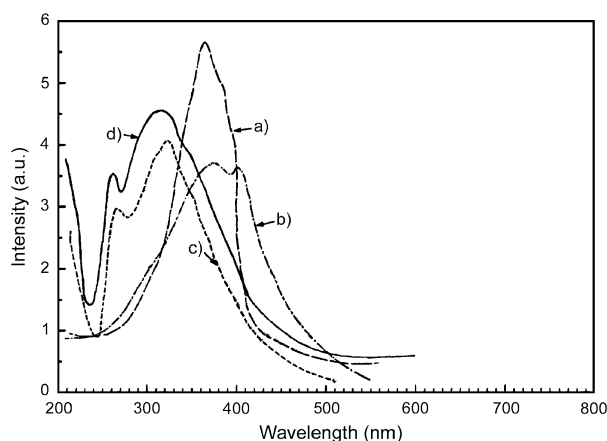


Scheme 1

Table 1. Properties of the Model and Polymeric Fluorophores

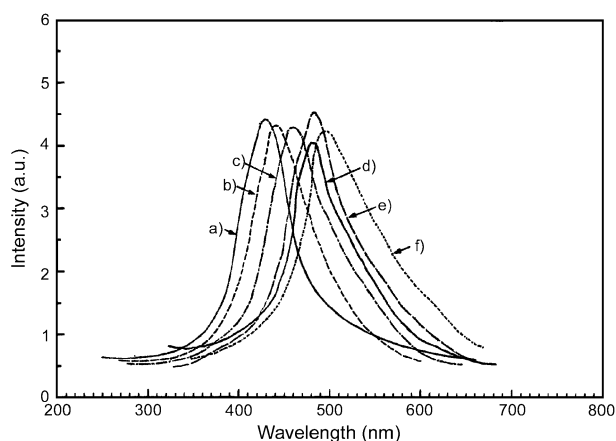
No	mp (°C)	η_{inh}^a	MW	MWD	Yield (%)
1	224-225	—	—	—	78
2	231	—	—	—	82
3	—	0.16	5100	1.6	85
4	—	0.23	7200	1.7	86

^aInherent viscosity was obtained at a concentration of 0.5 g/dL at 25°C

**Figure 1.** The UV-vis absorption spectra of a) 1, b) 2, c) 3 and d) 4.

The maximum absorption of **1** was shown at around 371 nm, which originated from fluorene unit. The UV-visible absorption spectrum of carbazole-containing fluorophores **2** and **4** were somewhat different from those of **1** and **3**. The maximum absorption showed a blue shift to 326 and 315 nm. The shoulders in the UV-vis spectra of **2** and **4** may be due to the formation of the excimer. The shapes of the spectrum obtained from the different concentrations were somewhat different from each other. The results of the investigation of PL for **1**, **2**, **3** and **4** are presented in the Figure 2. The spectra of the polymeric fluorophores are similar to those of the model fluorophores **1** and **2**. The PL spectrum of **4** with maximum showing a typical blue color at 477.3 nm appears.

Chemiluminescence. An aliquot of the hydrogen peroxide and sodium salicylate solution was added by bending to

**Figure 2.** Photoluminescence and chemiluminescence spectrum of a) **1** (PL), b) **1** (CL), c) **2** (PL), d) **2** (CL), e) **3** (PL) and f) **4** (CL).**Table 2.** The UV-vis Absorption, Photoluminescence and Chemiluminescence Maximum Wavelength of the Model and Polymeric Fluorophores

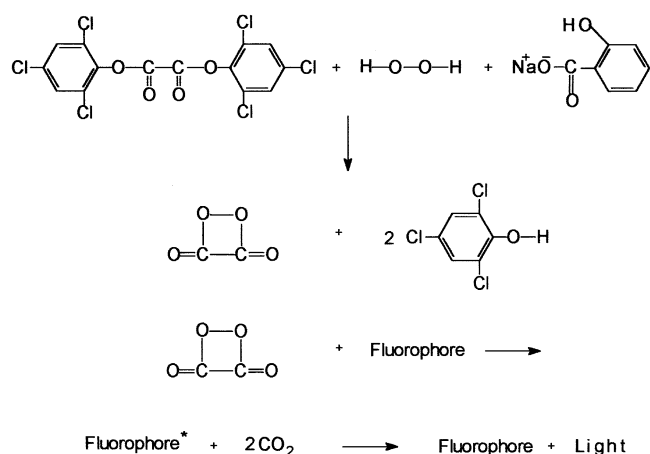
No	UV-vis ^a	PL ^b	CL ^c	Intensity Ratio ^d	
				(nm)	5 min
1	371.0	430.7	439.1	1.00	1.00
2	326.5	449.9	452.0	0.96	0.92
3	378.0	455.0	481.3	1.12	1.09
4	315.0	477.3	489.1	1.03	1.02

^aUV-vis spectra were obtained at a concentration of 10^{-4} – 10^{-5} mol/L. ^bPhotoluminescence in chloroform. ^cChemiluminescence in dibutyl phthalate. ^dThe ratio were determined by the relative intensity of the fluorophores and model compound **1** after 5 min and 30 min.

break the glass capillary containing fluorophore solution at 25 °C. It was found that the above model compounds and polymers were highly efficient fluorophores, which are highly soluble in the solvent system of the chemiluminescent reaction. As soon as the two components were mixed, the emission spectrum scanned immediately. The results of CL spectra obtained were similar to normal PL spectrum excited at 366 nm of ultraviolet light. Figure 2 showed chemiluminescence emission spectra of **1**, **2** and **4** centered around 439.1, 481.3 and 489.1 nm, respectively. Typical blue light emission has been observed from the CL of fluorophores since the wavelength of the emitted light is dependent on the conjugation length of the fluorophore, lowering this length will result in a blue shift in the emission.¹⁹ One way to achieve a blue-emitting polymer, therefore, is to interrupt the conjugation of the polymer at short intervals with non-conjugated segments. On the contrary, the substituents such as alkyl, alkoxy and halogen group made the fluorophores emit light at longer wavelength in the visible region. In the previous paper, polydistyrylarylene isolated with alkyl spacer showed blue emission ($\lambda_{max} = 470$ – 495 nm).^{12,13} In this experiment, fluorene- and carbazole-containing distyrylarylene polymers were moderate blue-emitting fluorophores without any spacer group and substituent.

In the peroxyoxalate chemiluminescence, the initial product does not emit light at all. It reacts with a fluorescence dye, and then the fluorophore becomes excited and emits light. One of the proposed reaction sequences in the reaction of peroxyoxalates, of which bis(2,4,6-trichlorophenyl)oxalate (TCPO) is the most prominent example, was illustrated in Scheme 2. It involves the fuel (TCPO) plus the oxidant (hydrogen peroxide) reacting to produce a proposed intermediate shown as 1,2-dioxetanedione. The fluorophores can be sidetracked along the way by loses in each step of the process: the initial oxidation the reaction of the intermediate with a fluorophore, and the reaction of the excited to produce light.²⁰

It is required that the fluorescence dye should be stable in the presence of hydrogen peroxide. The 1,2-diaryl-substituted ethylene (stilbene) unit was resistance to peroxide oxidation, therefore conjugated fluorophores emitted a blue light without change of wavelength during chemiluminescent reaction. The intensity of the chemiluminescence for



Scheme 2

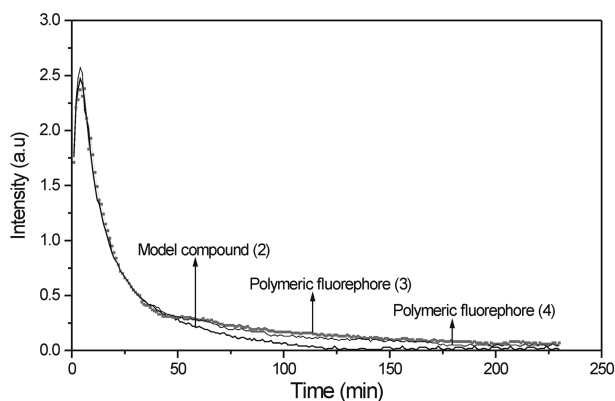


Figure 3. Decay of the chemiluminescent light intensity of model 3,6-distyryl-9-butylcarbazole (2) and polymeric fluorophores 3 and 4.

the model and polymeric fluorophores were showed in the Figure 3. The decay of the CL intensity from the maximum obeyed the following exponential equation.

$$y = 1.334e^{-x/t_1} + 0.437e^{-x/t_2}$$

$$t_1 = 14.49, t_2 = 101.72$$

It was found that fluorophores, which normally emit in the blue light region with good efficiency. The CL emission maintained for more than 12 hr and was visible with naked eye. The polymeric fluorophores showed similar light intensity to the model compounds as shown in Table 2. The energy transfer from the high energy level of less conjugated segments to the low energy level of more conjugated segments occurred in the polymeric fluorophore. The maximum brightness of CL is ca. 5000-5500 mcd/m² and 1500 and

200-300 mcd/m² after 30 min and 1 hr, respectively.

In the peroxyoxalate CL system, decay rate and maximum light intensity and efficiency depended on the concentration of hydrogen peroxide.²¹ In this experiment, 1.5 equivalent of hydrogen peroxide to TCPO was adopted.

In conclusion, fluorene- and carbazole-containing distyryl-arylene model and polymeric fluorophores were stable under peroxide oxidative condition. The fluorophores showed a typical blue light emission with 440-489 nm and was applicable to blue fluorescence dye for the chemiluminescence.

Acknowledgment. This work was supported by GRANT No.98-0502-10-01-3 from the Korea Science and Engineering Foundation.

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