

Chemiluminescence Properties of Polymeric Fluorophores Containing Distyrylarylene Unit

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Conjugated-non-conjugated alternating block copolymers containing distyrylarylene units were synthesized via Wittig reaction for chemiluminescent fluorophores. The polymers were differentiated from others by the presence of aromatic unit in the chromophoric block. When UV-VIS, photoluminescence and chemiluminescence spectra of these materials were compared with copolymers, a strong bathochromic effect was observed. A more pronounced red shift and higher chemiluminescence efficiency were observed in the polymer with anthracene ring. Sodium salicylate-catalyzed reaction of bis(2-carboxypentyloxy-3,5,6-trichlorophenyl) oxalate with hydrogen peroxide produced a strong chemiluminescence from blue to yellow-green light emission with wavelength of 450-537 nm in the presence of the fluorophore. The chemiluminescent intensity decayed exponentially. The glow of chemiluminescence maintained more than 12 hr and was visible with the naked eye.

Keywords : Polymeric fluorophore, Chemiluminescence, Distyrylarylene polymer, Copolymerization, Color tuning.

Introduction

The production of chemiluminescent light by the reaction of a catalyzed hydrogen peroxide solution with a fluorophore solution is well known.¹⁻⁶ Recent advances in chemiluminescence have created a need for new fluorophores with various colorations. In the case of chemiluminescent emission, a simple blending of several chromophores produced a corresponding new color.⁷ Conventional chemiluminescent fluorophores were highly conjugated aromatic compounds such as perylene, rubrene, 9,10-diphenylanthracene and 9,10-bis(phenylethynyl)anthracene derivatives.⁸

The commercially available chemiluminescent light devices or system fail to prevent pollution of fluorophore after finishing the glow of a light source. A particular class of fluorophores of interest is the π -conjugated polymers, which are generally more tractable, stable and less toxic than conventional molecular fluorophores. A few examples appeared in the literature applying the polymeric fluorophores to chemiluminescent reaction through intermolecular chemical energy-transfer processes.⁹⁻¹² Various polydistyrylarylenes containing 1,4-bis(2',2'-diphenylvinyl)benzene, 1,4-bis(2'-phenylvinyl)benzene,⁹ fluorene and carbazole units¹¹ were adopted as the blue light-emitting chemiluminescence fluorophores. More recently, it was reported that perylene tetracarboxydiimide-containing polyester and polyurethane were used as an efficient red color (625 nm) light-emitting fluorophores during chemiluminescence reaction.¹²

In this report, distyrylarylene-containing polymeric fluorophores, in which different chromophores were combined and color tuning can be accomplished by copolycondensation, were prepared and their chemiluminescent characteristics including various optical properties were examined.

Experimental Section

Chemicals and Instruments. The dialdehyde, 1,6-bis(4-formyl-3,5-dimethoxyphenyleneoxy)hexane was synthesized according to the procedure previously reported.^{13,14} 1,4-Xylylene-bis(triphenylphosphonium chloride), 4,4'-bis(chloromethyl)biphenyl triphenylphosphonium salt and 9,10-bis(chloromethyl)anthracene triphenylphosphonium salt were prepared from the corresponding dihalides and triphenyl phosphine by the literature method reported by Karasz *et al.*^{13,14} Bis(2-carboxypentyloxy-3,5,6-trichlorophenyl)oxalate (CPPO) was prepared by the method described previously.¹⁵ Sodium salicylate, *tert*-butanol, dibutylphthalate (GR, Yakuri Co.) and dimethylphthalate (GR, Junsei Chem. Co.) were used without further purification. Hydrogen peroxide (35%) was concentrated to *ca.* 90% by using anhydrous magnesium sulfate prior to use. 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. Gel-permeation chromatography (GPC) data were obtained with a Waters HPLC using three columns (μ -Stryragel 10², 10³ and 10⁴ Å) in THF and calibrated with polystyrene standards at 20 °C. Intrinsic viscosity of polymer solutions was measured in a Ubbelohde viscometer at 25 °C in dimethylphthalate. 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 Polymers with Distyrylarylene Units. A solution of 1,6-bis(4-formyl-3,5-dimeth-

oxyphenyleneoxy)hexane (2.84 g, 6.0 mmol), 1,4-xylylene-bis(triphenylphosphonium chloride) (3.01 g, 3.0 mmol) and 9,10-bis(chloromethyl)anthracene triphenylphosphonium salt (2.23 g, 3.0 mmol) in a mixture of anhydrous methanol and tetrahydrofuran (v/v = 50/50, 60 mL) was placed in a Schlenk flask and degassed, then stirred under a gentle flow of nitrogen. A 25 wt% solution of sodium methoxide in methanol (2.8 mL, 12 mmol) was added dropwise using a long steel needle and syringe. The reaction turned yellow and a slurry was produced in a few minutes. After 3 hr, the reaction was quenched by addition of methanol (200 mL) and acidified with concentrated hydrochloric acid (10 mL). The polymer obtained was purified by successive precipitation until no color was observed in the mother liquid. The sample was dried in a vacuum oven at room temperature for 24 hr.

The other polymers **1**, **2**, **3**, **4** and **6** were prepared by a similar method described above.

1: Yield 87%. IR (KBr): 3070-3020 (aromatic C-H), 2870 (aliphatic C-H), 1639 (C=C), 1250-1050 (C-O) and 960 (-C=C-H) cm^{-1} . ^1H NMR (CDCl_3): δ = 7.60-7.05 (m, 8H, aromatic protons) 7.0 (m, 4H, vinyl protons), 4.02 (t, 4H, 2 -OCH₂-), 1.35 (m, 8H, -CH₂-CH₂-CH₂-CH₂-). Anal. Calcd for C₃₂H₃₆O₆ (426); C, 62.74; H, 5.88. Found: C, 62.58; H, 5.79.

2: Yield 83%. IR (KBr): 3080-3010 (aromatic C-H), 2870-2880 (aliphatic C-H), 1640 (C=C), 1250-1050 (C-O) and 961 (-C=C-H) cm^{-1} . ^1H NMR (CDCl_3): δ = 7.60-7.00 (m, 16 H, aromatic protons) 7.0 (m, 4H, vinyl protons), 4.02 (t, 4H, 2 -OCH₂-), 1.35 (m, 8H, -CH₂-CH₂-CH₂-CH₂-). Anal. Calcd for C₃₆H₄₀O₆(568); C, 76.06; H, 7.04. Found: C, 75.78; H, 7.01.

3: Yield 85%. IR (KBr): 3070-3010 (aromatic C-H), 2880 (aliphatic C-H), 1639 (C=C), 1250-1050 (C-O) and 960 (-C=C-H) cm^{-1} . ^1H NMR (CDCl_3): δ = 7.60-7.05 (m, 12H, aromatic protons) 7.0 (m, 4H, vinyl protons), 4.02 (t, 4H, 2 -OCH₂-), 1.35 (m, 8H, -CH₂-CH₂-CH₂-CH₂-). Anal. Calcd for C₄₀H₄₀O₆(616); C, 77.92; H, 6.49. Found: C, 77.76; H, 6.29.

4: Yield 77%. IR (KBr): 3080-3020 (aromatic C-H), 2880 (aliphatic C-H), 1640 (C=C), 1250-1020 (C-O) and 960 (-C=C-H) cm^{-1} . ^1H NMR (CDCl_3): δ = 7.60-7.05 (m, aromatic protons) 7.0 (m, vinyl protons), 4.02 (t, 4H, 2 -OCH₂-), 1.35 (m, 8H, -CH₂-CH₂-CH₂-CH₂-). Anal. Calcd for C₃₅H₃₈O₆ (554); C, 75.81; H, 6.86. Found: C, 75.58; H, 6.79.

5: Yield 76%. IR (KBr): 3080-3020 (aromatic C-H), 2880 (aliphatic C-H), 1640 (C=C), 1250-1050 (C-O) and 960 (-C=C-H) cm^{-1} . ^1H NMR (CDCl_3): δ = 7.60-7.00 (m, aromatic protons) 7.0 (m, vinyl protons), 4.00 (t, 4H, 2 -OCH₂-), 1.36 (m, 8H, -CH₂-CH₂-CH₂-CH₂-). Anal. Calcd for C₃₆H₃₈O₆ (566); C, 76.33; H, 6.71. Found: C, 75.98; H, 7.52.

6: Yield 72%. IR (KBr): 3070-3020 (aromatic C-H), 2880 (aliphatic C-H), 1640 (C=C), 1250-1050 (C-O) and 960 (-C=C-H) cm^{-1} . ^1H NMR (CDCl_3): δ = 7.60-7.00 (m, aromatic protons) 7.0 (m, vinyl protons), 4.03 (t, 4H, 2 -OCH₂-), 1.34 (m, 8H, -CH₂-CH₂-CH₂-CH₂-). Anal. Calcd for C₃₉H₄₀O₆ (604); C, 77.48; H, 6.62. Found: C, 77.21; H, 6.39.

Preparation of Chemiluminescent Solution. Model fluorophore (0.3 wt%) and bis(2-carbopentyloxy-3,5,6-trichlorophenyl)oxalate (CPPO, 20 mmol) were dissolved in dibutylphthalate (200 mL) at 80 °C under nitrogen. The catalyst solution, hydrogen peroxide (95%, 1.5 equivalent of CPPO) and sodium salicylate (0.25 mmol) were dissolved in 20 mL of mixed solvent of dimethylphthalate/*tert*-butanol (3/2). The chemiluminescence was measured by mixing fluorophore solution (0.9 mL) and hydrogen peroxide solution (0.3 mL).

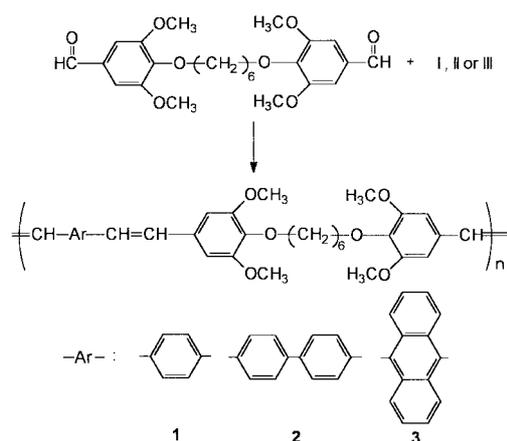
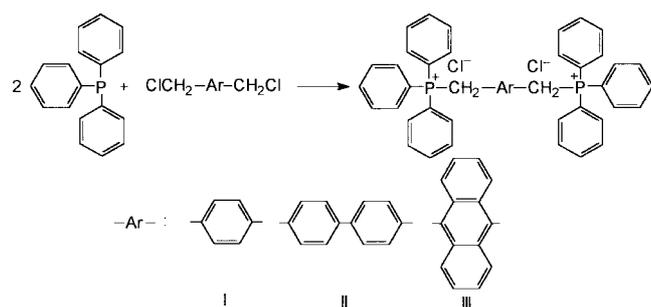
Measurements of Chemiluminescence. Rates of catalytic decomposition of CPPO were determined by monitoring the decay intensity of chemiluminescent fluorophore solutions. A cylindrical polypropylene tube (ID, 4 mm; L, 50 mm) was filled with hydrogen peroxide solution (0.3 mL) and a glass capillary containing fluorophore solution (0.9 mL), and sealed with a melted polypropylene. The sample was bent to break and placed in the thermostatic sample block of the chemiluminescence-measuring luminometer. Measurement of the signal was started from opening the shutter. The chemiluminescence decay was generally recorded for at least 12 hr.

Results and Discussion

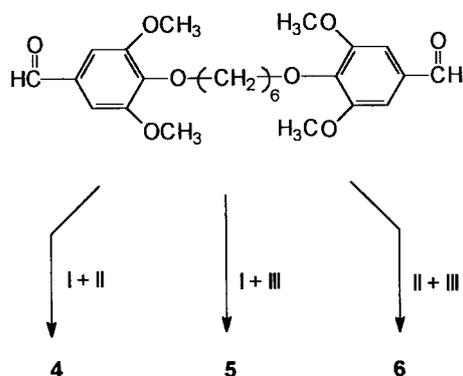
Preparation and Characterization of Polymeric Fluorophores. Dialdehyde monomer 1,6-bis(4-formyl-1,5-dimethoxyphenyleneoxy)hexane, 1,4-xylylene-bis(triphenylphosphonium chloride), 4,4'-bis(chloromethyl)biphenyl triphenylphosphonium salt and 9,10-bis(chloromethyl)anthracene triphenylphosphonium salt were selected for the preparation of distyrylarylene polymeric fluorophore. Polymer **1**, which was previously synthesized, represents the reference structure for comparison with the new polymers. The Wittig-type polycondensation, used to synthesize polymers, was easily accomplished by the reaction between dialdehyde and the ylide, which was formed in situ from the reaction between sodium methoxide and the corresponding phosphonium salt as illustrated in Scheme 1.

The homopolymers were isomerized to all-*trans* configuration by refluxing the polymer solution in toluene with a catalytic amount of iodine. Three copolymers were also prepared by reacting two of the three monomers containing phosphonium salt with 1,6-(4-formyl-1,5-dimethoxyphenyleneoxy)hexane. We could obtain all of the polymeric fluorophores in high yield. Scheme 2 and Table 1 summarize the results of the preparation of polymeric fluorophores.

The fluorophores were characterized through the data from proton NMR, IR and elemental analyses. In the FT-IR spectra of the polymer samples, a peak was found in the 920-960 cm^{-1} region attributable to the out-of-plane vibration of the *trans* vinylene groups of the fluorophore. In the aliphatic regions of the ^1H NMR spectra, all samples showed at 4.05, 3.90 and 1.75-1.26 ppm assignable to -OCH₂-, -OCH₃ and -(CH₂)₄-, respectively. The doublet at 7.04 ppm was corresponding to the *trans*-vinylene protons. A very small peak at 10.1 ppm is attributed to the terminal aldehyde groups. The CHN analysis values matched well with the data calculated



Scheme 1



Scheme 2

Table 1. Results of Polymerization of Polymeric Fluorophores 1-6

Polymers	Monomer ^a	MW	Mw/Mn (MWD)	Yield (%)
1	I	9700	2.2	87
2	II	15400	3.59	83
3	III	3200	1.01	85
4	I + II	12700	1.55	77
5	I + III	7600	2.26	76
6	II + III	7000	2.24	72

^aI, 1,4-xylylene-bis(triphenylphosphonium chloride); II, 4,4'-bis(chloromethyl)biphenyl triphenylphosphonium salt; III, 9,10-bis(chloromethyl)anthracene triphenylphosphonium salt.

from the expected chemical structure. The weight average molecular weights (Mw) of polymers 1-6 were between

3200 and 15400 with a molecular weight distribution of 1.01 and 3.59. Data from the GPC analysis are shown in Table 1. Polymers 3 showed quite a low molecular weight. This can be attributed to the solubility of 9,10-bis(chloromethyl)anthracene triphenylphosphonium salt in tetrahydrofuran as a reaction medium. The polymer was precipitated in tetrahydrofuran during the polycondensation.

Polymers were soluble in common organic solvents such as chloroform, tetrahydrofuran and dibutylphthalate. The solubility data are summarized in Table 2.

Optical Properties. Optical properties of a series of copolymers 4-5 in dilute solution were measured and compared with those of the corresponding model polymers 1-3. The UV absorbance, photoluminescence as well as the chemiluminescence characteristics of polymeric fluorophores were measured and listed in Table 3. The characteristic maximum absorption of 1, 2 and 3 were shown at 353, 357 and 398 nm, respectively. The absorption spectra of copolymers 4-6 showed a peak centered around 360 nm. In the case of copolymers 5 and 6, a pronounced bathochromic effect can be obtained when the anthracene moiety was incorporated by copolymerization.

The results of the investigation of photoluminescence for polymers 1-6 are presented in the Figure 1. The photoluminescence spectrum of 1, 2 and 4 exhibited blue color with wavelength of 445-450 nm, while polymer 3 showed a greenish-yellow emission at 535 nm.

Table 2. Solubility of Polymeric Fluorophores 1-6

Polymers	DMSO DMF	THF	CHCl ₃	DBP	EtOH	Bz	Hexane
1	++	++	++	++	+	+	-
2	+	++	++	++	+	-	-
3	-	+	+	+	-	-	-
4	+	++	++	++	+	-	-
5	+	++	++	++	-	-	-
6	-	+	+	+	-	-	-

Table 3. The UV-Vis Absorption, Photoluminescence and Chemiluminescence Maximum Wavelength of the Polymeric Fluorophores

Polymers	UV (λ _{max}) ^a	PL (λ _{max}) ^a	CL (λ _{max}) ^a	CIE Color Coordinate
1	353	445	450	X=0.16 Y=0.26
2	357	450	452	X=0.20 Y=0.24
3	398	535	537	X=0.35 Y=0.50
4	359	449	451	X=0.18 Y=0.22
5	362	499	501	X=0.25 Y=0.36
6	364	503	504	X=0.26 Y=0.35

^aMeasured in dibutylphthalate solution.

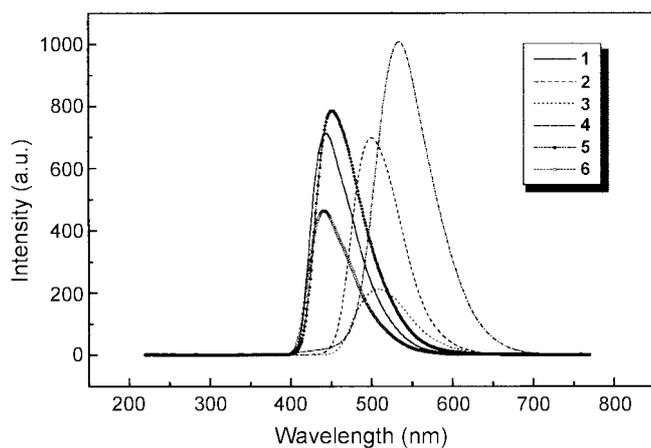


Figure 1. Photoluminescence spectra of polymeric fluorophores 1-6.

Chemiluminescence. Typical chemiluminescence studies were performed by combining a solution of fluorophore and CPPO with a solution of the catalyst and hydrogen peroxide at 25 °C. Chemiluminescence devices can be easily prepared by adding the solution of catalyst and hydrogen peroxide to the polypropylene tube. A sealed glass capillary tube containing fluorophore and CPPO is then placed in the solution of catalyst and hydrogen peroxide in the tube, which is then sealed. Chemiluminescence occurs, when the tube is bent. The capillary tube is broken and the mixture is shaken for 1 min. The fluorophore solution is activated instantly by the catalyst solution. It was observed that all the polymers were highly efficient fluorophores, which are moderately soluble in the solvent system of the chemiluminescent reaction. The emission spectrum scanned at 2 min after the two components were mixed. The results of chemiluminescence spectra obtained were similar to normal photoluminescence spectrum excited at 366 nm of ultraviolet light. Chemiluminescence emissions spectra of 1-4 appeared between 450 and 537 nm as shown in Figure 2. Blue and yellow-green light emission have been observed from the chemiluminescence of fluorophores 1 and 3, respectively, since the

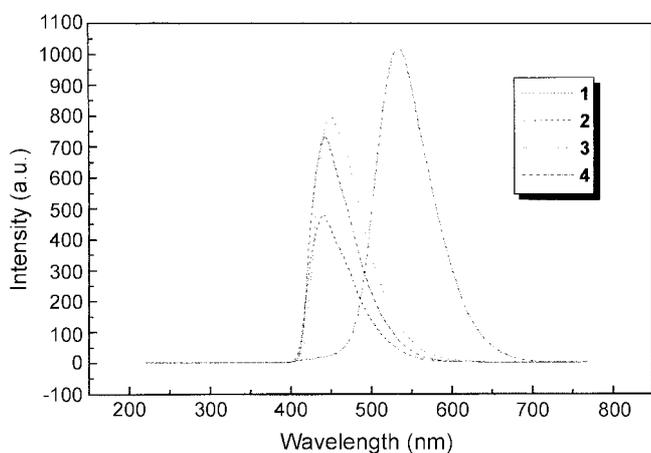


Figure 2. Chemiluminescence spectra of polymeric fluorophores 1-4.

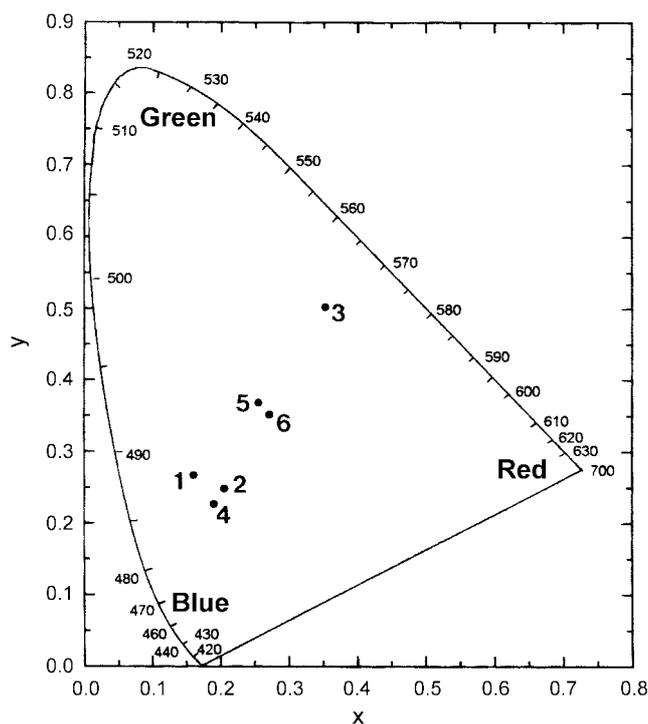


Figure 3. CIE chromaticity Diagram of the chemiluminescence of polymeric fluorophores 1-6.

wavelength of the emitted light is dependent on the conjugation length of the fluorophore.¹⁶ In the previous paper, polydistyrylarylene isolated with alkyl spacer showed blue emission ($\lambda_{\text{max}} = 470\text{-}495\text{ nm}$).^{9,11} In this experiment, polymers 5 and 6 having anthracene moiety were moderate white-blue light-emitting fluorophores. Figure 3 shows a chemiluminescence emission light of fluorophore 1-6 in the CIE chromaticity diagram.

It is required that the fluorescent dye should be stable in the presence of hydrogen peroxide. The 1,2-diaryl-substituted ethylene(stilbene) unit was resistance to peroxide oxidation, conjugated fluorophores emitted a light with small change of CIE chromaticity value from $x = 0.16$, $y = 0.20$ to $x = 0.18$, $y = 0.23$ during chemiluminescent reaction.

A typical chemiluminescence decay curve for all the polymeric fluorophores in DBP shows a rapid decay during the first 30 minutes followed by a much slower decay lasting over 12 hr. A similar, but much brighter chemiluminescence pattern was observed for anthracene-containing polymers. While the origin of the distinctive decay mode is well-defined at this time, we speculate that the initial burst results from and is controlled by the rate of release of the peroxyoxalate which then reacts rapidly with the fluorophore.¹⁻⁶ These decay profiles can be fitted to exponential rate curve and accord with the intermediate model.

The decay intensities of the chemiluminescence for the polymeric fluorophores are showed in Figure 4. Chemiluminescence emission was maintained for more than 12 hr and was visible with the naked eye. The energy transfer from the high energy level of less conjugated segments to the low energy level of more conjugated segments occurred in the

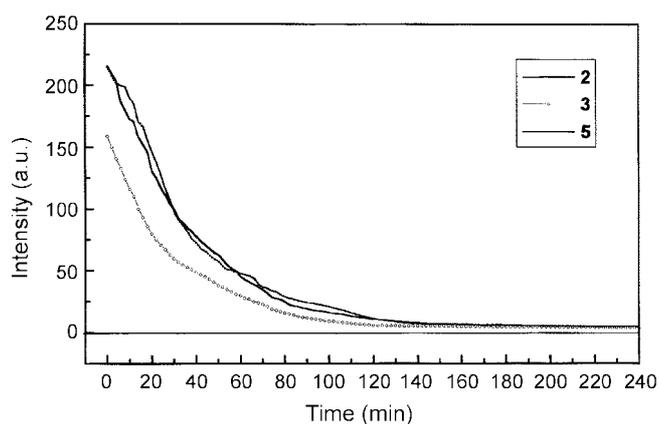


Figure 4. Decay of the chemiluminescent light intensity of polymeric fluorophore 2, 3 and 5.

polymeric fluorophore. The maximum brightness of CL is ca. 45-60 cd/cm² and 10-15 cd/cm² after 5 min and 1 hr, respectively.

In conclusion, distyrylarylene-containing polymeric fluorophores were applicable to blue, white-blue and yellow-green fluorescent dye for the chemiluminescence and stable under peroxide oxidative condition. The color of fluorophores can be tuned by the copolymerization of monomers containing chromophore units.

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