Chemiluminescent Properties of Novel Biphenyl Analogue Blue Fluorophores

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Received June 1, 2004

Novel naphthyl-containing biphenyl analogues were prepared by Suzki reaction for the chemiluminescent blue fluorophores. UV-Vis absorption, photoluminescence, chemiluminescence and CIE chromaticities were measured. The fluorophores displayed blue photoluminescence in solution with a maximum intensity around 378-415 nm. Sodium salicylate-catalyzed reaction of them with bis(2-carbopentyloxy-3,5,6-trichlorophenyl)-oxalate with hydrogen peroxide provided a strong chemiluminescent red light emission with wavelengths of 398-427 nm; these were similar to the photoluminescent spectra. The chemiluminescent intensity decayed exponentially and the glow of chemiluminescence, which was visible with naked eyes, was maintained for more than 4 h.

Key Words : 4,4'-Di(1-naphthyl)biphenyl, 2,7-Di(1-naphthyl)fluorene, 3,6-Di(2-naphthyl)carbazole, Blue fluorophore, Chemiluminescence

Introduction

The unique properties of the peroxyoxalate chemiluminescent system permit many applications which cannot be served by electrically powered devices.[1] Because of its cold nature, chemical light can be employed safely in areas where the possibility of explosion exist. A variety of uses has been developed in recent years: emergency lights during power failures; small portable lights for camping, backpacking, and jogging; marking lights for life jacket; lures for commercial fishing; and a wide spectrum of novel uses.[2]

Several different chemiluminescent fluorophores were employed to produce different colors[2-7]: *N,N'*-bis(2,6-diisopropylphenyl)-1,6,7,12-tetrakis(*p-tert*-butylphenoxy)-3,4,9,10-perylenetetracarboxydiimide (red), rubrene (red), 2-chloro-9,10-bis(*p*-methoxyphenyl)anthracene (blue), 9,10-bis(phenylethynyl)anthracene (green) and 1-chloro-9,10-bis(phenylethynyl)-2-chloroanthracene (yellow) are among them.

9,10-Diphenylanthracene derivatives especially have been widely used in commercial and industrial applications because of their stability in peroxide oxidative conditions.[8,9] In recent years, blue fluorophore 2-chloro-9,10-bis(*p*-methoxyphenyl)anthracene have been applied in chemiluminescent reactions.[8-11] Methoxy and chloro substituents can tune the color, and increase solubility required as a chemiluminescent fluorophore.

In this report, various naphthalene-containing biphenyl analogues such as biphenyl, fluorene and carbazole were prepared and their chemiluminescent characteristics were examined and evaluated.

Experimental Section

Chemicals and instruments. 4,4'-Di(1-naphthyl)biphenyl (**1**), 4,4'-bis[2-(6-methoxynaphthyl)]biphenyl (**2**) and 2,7-di(1-naphthyl)fluorene (**3**) were prepared by the method previously reported.[12-14] 4,4'-Dibromobiphenyl, 1-naphthaleneboronic acid, 6-methoxy-2-naphthaleneboronic acid and 2-naphthaleneboronic acid (Aldrich Chem. Co.) were used without further purification. Potassium carbonate (Aldrich Chem. Co.), sodium salicylate (Aldrich Chem. Co.), *t*-butanol, dibutylphthalate (GR, Yakuri Co.) and dimethylphthalate (GR, Junsei Chem.Co.) were used without further purification.

2-Chloro-9,10-di(*p*-methoxyphenyl)anthracene and bis(2-carbopentyloxy-3,5,6-trichlorophenyl)oxalate (CPPO, RGB Chem. Co.) were used as received. Sodium salicylate (Aldrich Chem. Co.), *t*-butanol, dibutylphthalate (GR, Yakuri Co.) and dimethylphthalate (GR, Junsei Chem. Co.) were used without further purification.

UV-Vis spectra were obtained by Shimadzu UV/vis spectrophotometer UV-1601PC. Intensity of the emission was measured with a Minolta Chromameter CS-l00. Photoluminescence was measured on a Shimadzu fluorophotometer RF-5301PC.

4,4'-Di(1-naphthyl)biphenyl (1). To a mixture of 4,4'-dibromobiphenyl (1 g, 3.205 mmol), 1-naphthaleneboronic acid (1.213 g, 7.051 mmol) and K_2CO_3 (1 M aqueous solution, 70 mL) dissolved in anhydrous THF (60 mL), was added $Pd(PPh_3)_4$ (0.163 g, 0.141 mmol) dissolved in anhydrous THF (30 mL) under nitrogen. After the resulting mixture was refluxed for 24 h, the organic layer was separated and diluted with dichloromethane (100 mL). The solution was then washed with 1 N HCl (30 mL) and brine (30 mL). After the solvent was removed, the crude solid product was recrystallized in ethyl acetate. Similar experimental procedures were adopted for the preparation of other fluorophores, 4,4'-bis[2-(6-methoxynaphthyl)]biphenyl (**2**), 2,7-di(1-naphthyl)-fluorene (**3**), 9,9-dibutyl-2,7-bis[2-(6-methoxynaphthyl)]-fluorene (**4**), 9-butyl-3,6-di(1-naphthyl)carbazole (**5**), 9-butyl-3,6-di(1-naphthyl)carbazole (**6**), and 9-butyl-3,6-

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[bis(6-methoxynaphthyl)]carbazole (**7**).

1: Yield: 53%. mp: 176-177 °C. FT-IR (KBr, cm^{-1}) 3045 (aromatic C-H). ^{13}C NMR ($CDCl_3$) δ 125.24, 125.63, 125.82, 125.92, 126.76, 127.54, 128.13, 130.37, 131.37, 133.61, 139.56. ^1H NMR ($CDCl_3$) δ 8.05-7.48 (m, 22 H, aromatics). Anal. Calcd for $C_{32}H_{22}$ (Mw, 406.528): C, 94.54; H, 5.46. Found: C, 94.36; H, 5.39.

2: Yield: 41%. mp: 259-260 °C. FT-IR (KBr, cm^{-1}) 3046 (aromatic C-H), 1000 (ether C-O). ^{13}C NMR ($CDCl_3$) δ 53.80, 103.92, 116.70, 123.79, 124.14, 125.93, 126.54, 126.91, 128.36, 130.20, 136.17, 156.22. ^1H NMR ($CDCl_3$) δ 7.14-8.05 (m, 20H, aromatics), 3.94 (s, 6H, methoxy). Anal. Calcd for $C_{34}H_{26}O_2$ (Mw, 466.580): C, 87.53; H, 5.62. Found:C, 87.66; H, 5.49.

3: Yield: 65%. mp: 184-185 °C. FT-IR (KBr, cm^{-1}) 3060 (aromatic C-H), 2900 (aliphatic C-H) cm^{-1}. ^1H NMR ($CDCl_3$) δ 8.12-7.25 (m, 20H, aromatics) 4.1 (t, 2H, benzyl proton). Anal. Calcd for $C_{33}H_{22}$ (Mw, 418.539): C, 94.70; H, 5.30. Found: C, 94.47; H, 5.34.

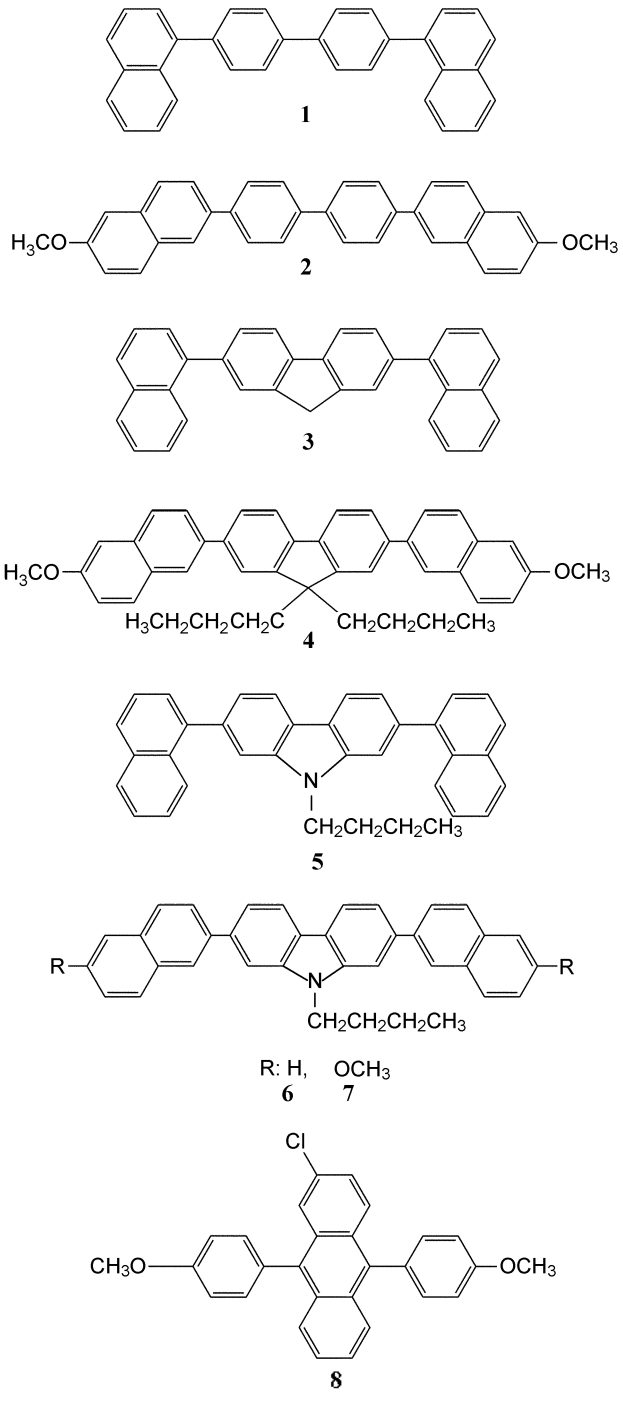
4: Yield: 43%. mp: 68-69 °C. FT-IR (KBr, cm^{-1}) 3046 (aromatic C-H) 2945, 2854 (aliphatic C-H). ^{13}C NMR ($CDCl_3$) δ 23.22, 26.40, 40.14, 55.20, 124.66, 125.23, 125.88, 126.74, 127.35, 128.14, 128.66, 131.75, 133.68, 139.25, 139.75, 140.47. ^1H NMR ($CDCl_3$) δ 7.28-8.05 (m, 20H, aromatics), 2.02 (t, 2H, C-C*H*$_2$-), 0.89 (m, 2H, C-CH$_2$C*H*$_2$-), 1.25 (m, 2H, -C*H*$_2$CH$_3$), 0.74 (t, 3H, -C*H*$_3$). Anal. Calcd for $C_{41}H_{42}$ (Mw, 566.785): C, 86.88; H, 7.47. Found: C, 86.76; H, 7.49.

5: Yield: 46%. mp: 142-143 °C. FT-IR (KBr, cm^{-1}) 3035 (aromatic C-H), 2952 (aliphatic C-H), 1209 (amine C-N). ^{13}C NMR ($CDCl_3$) δ 13.62, 20.01, 31.66, 44.50, 120.98, 123.13, 124.98, 125.25, 125.47, 125.76, 126.09, 126.23, 127.01, 127.28, 128.04, 131.25, 131.96, 133.67, 140.59. ^1H NMR ($CDCl_3$) δ 7.36-8.32 (m, 20H, aromatics), 3.66 (t, 2H, =N-C*H*$_2$-), 1.26 (m, 2H, N-CH$_2$-C*H*$_2$-), 0.68 (m, 2H, -C*H*$_2$-CH$_3$), 0.47 (t, 3H, -C*H*$_3$). Anal. Calcd for $C_{36}H_{29}N$ (Mw, 475.635): C, 90.91; H, 6.15; N, 2.94. Found: C, 90.83; H, 6.17; N, 2.89.

6: Yield: 68%. mp: 160-161 °C. FT-IR (KBr, cm^{-1}) 3050 (aromatic C-H), 2952 (aliphatic C-H), 1208 (amine C-N). ^{13}C NMR ($CDCl_3$) δ 13.63, 19.95, 31.20, 44.62, 109.71, 118.00, 118.86, 123.72, 125.35, 125.86, 126.01, 126.41, 127.44, 127.62, 127.96, 128.25, 128.44, 131.70, 132.11, 132.42, 132.83, 133.69, 138.57, 141.23. ^1H NMR ($CDCl_3$) δ 7.18-8.57 (m, 20H, aromatics), 3.87 (t, 2H, =N-C*H*$_2$-), 1.44 (m, 2H, N-CH$_2$-C*H*$_2$-), 0.72 (m, 2H, -C*H*$_2$-CH$_3$), 0.51 (t, 3H, -C*H*$_3$). Anal. Calcd for $C_{36}H_{29}N$ (Mw, 475.635): C, 90.91; H, 6.15; N, 2.94. Found: C, 90.93; H, 6.13; N, 2.89.

7: Yield: 41%. mp: 128-129 °C. FT-IR (KBr, cm^{-1}) 3050 (aromatic C-H), 2940 (aliphatic C-H), 12038 (amine C-N), 1020 (ether C-O). ^{13}C NMR ($CDCl_3$) δ 13.69, 19.98, 31.21, 44.63, 55.40, 105.50, 109.63, 118.59, 119.25, 124.97, 125.34, 126.24, 127.02, 128.33, 129.21, 131.77, 133.12, 133.58, 136.51, 137.39, 157.17. ^1H NMR ($CDCl_3$) δ 7.12-8.53 (m, 18H, aromatics), 3.95 (t, 2H, =N-C*H*$_2$-), 3.93 (s, 6H, methoxy) 1.43 (m, 2H, N-CH$_2$-C*H*$_2$-), 0.73 (m, 2H, -C*H*$_2$-CH$_3$), 0.54 (t, 3H, -C*H*$_3$). Anal. Calcd for $C_{38}H_{33}N$ (Mw, 503.689): C, 90.61; H, 6.60; N, 2.78. Found: C, 90.45; H, 6.55; N, 2.71.

Measurements of chemiluminescent decay time. Fluorophore **4** (10^{-3} M) and CPPO (3.90×10^{-3} M) were dissolved in dibutylphthalate at 80 under nitrogen. On the other hand, hydrogen peroxide (90%, 1.5 equivalent of CPPO) and sodium salicylate (2.5×10^{-5} M) were dissolved in dimethylphthalate/*t*-butanol (v/v, 4/1). Chemiluminescent spectra and the rates of catalytic decomposition were obtained by conducting the reactions in a quartz cuvette of spectrometer. The hydrogen peroxide solution (0.6 mL) was poured to the



Scheme 1

Table 1. Results of preparation of naphthalene-containing biphenyl analogue fluorophores

Fluorophores	Mp (°C)	Dihedral Angles (Deg)		Yields (%)
		B-B[a]	B-N[b]	
1	176-177	72.256	49.144 / 48.850	53
2	259-260	0.316	1.38 / 0.45	41
3	184	0	49.34 / 49.18	52
4	69	0	55.23 / 59.41	55
5	142-143	0	51.58 / 51.02	46
6	161	0	33.23 / 4.39	68
7	128	0	34.93 / 29.99	41
8[c]	212	–	–	87

[a]Dihedral angles between two phenyl groups in biphenyl analogues. [b]Dihedral angles between biphenyl analogues and naphthyl group. [c]2-chloro-9,10-di(*p*-methoxyphenyl)anthracene.

Table 2. The UV-vis absorption, photoluminescent and chemiluminescent maximum wavelength of the naphthalene-containing biphenyl analogues

Fluoro-phores	UV (λ_{max})[a]	PL (λ_{max}) at 366 nm[b]	Color (Solid state)	CL (λ_{max})[c]
1	260 / 335	380	Pale yellow	401
2	279 / 331	377	Pale yellow	398
3	241 / 341	380	White	390
4	269 / 350	407	Pale yellow	397
5	280 / 349	387	Pale yellow	420
6	295 / 359	409	Pale yellow	421
7	291 / 356	415	Pale yellow	427
8	400	439	Pale yellow	453

[a]Measured in chloroform solution. [b]Measured using irradiating the maximum absorption wavelength in dibutylphthalate solution. [c]Measured during chemiluminescent reaction.

cuvette filled with a fresh fluorophore solution (1.8 mL). Chemiluminescent decay was recorded just after 1 min by opening the shutter.

Results and Discussion

Preparation and characterization of blue fluorophores. Various biphenyl analogue blue fluorophores containing naphthalene unit were synthesized by Suzuki reactions.[15-20] They were easily synthesized by the reaction of 4,4'-dibromobiphenyl, 2,7-dibromo-fluorene, 2,7-dibromo-9,9-dibutylfluorene and 9-butyl-3,6-dibromocarbazole with corresponding boric acid derivative in the presence of tetrakis(triphenylphosphine)palladium(0) and potassium carbonate as illustrated in Scheme 1.

Table 1 summarizes the results of the preparation of fluorophores, 4,4'-di(1-naphthyl)biphenyl (**1**), 4,4'-bis[2-(6-methoxynaphthyl)]biphenyl (**2**), 2,7-di(1-naphthyl)fluorene (**3**), 9,9-dibutyl-2,7-bis[2-(6-methoxynaphthyl)]fluorene (**4**), 9-butyl-3,6-di(1-naphthyl)carbazole (**5**), 9-butyl-3,6-di(1-naphthyl)carbazole (**6**) and 9-butyl-3,6-[bis(6-methoxy-naphthyl)]carbazole (**7**). A comparison of above fluorophores with commercial blue fluorophore 2-chloro-9,10-di(*p*-methoxyphenyl)anthracene (**8**) was performed.

All the fluorophores were soluble in common organic solvents such as chloroform, tetrahydrofuran and dibutylphthalate. It was noted that fluorene- and carbazole-based fluorophores **3-7** showed a greater solubility than **1** and **2** because the incorporation of alkyl group into the fluorene and carbazole moiety enhanced the solubility in common organic solvents to a higher degree.

They are blue fluorophores with deformations in geometry. Thus the geometric characteristics were determined by means of the CS Chem 3D Pro v. 5.0 modeling system. The data present the optimized geometries after energy minimization. The calculations were carried out with full geometry optimization (dihedral angle). It seems that fluorophore **1** deviated significantly from the coplanar conformation. Particularly, dihedral angle between two phenyl groups was 72.26° for **1** and 0.32° for **2**. In addition, the twist angles between the biphenyl and the adjacent naphthyl group were 1.38° and 55.23° for compound **2** and **4**, respectively. In the case of compounds **5-7** with carbazole moiety, the dihedral angle of α-naphthyl group also showed larger than that of β-naphthyl group. This would result in the release of the crowding of bonded substituent in the dye molecule.

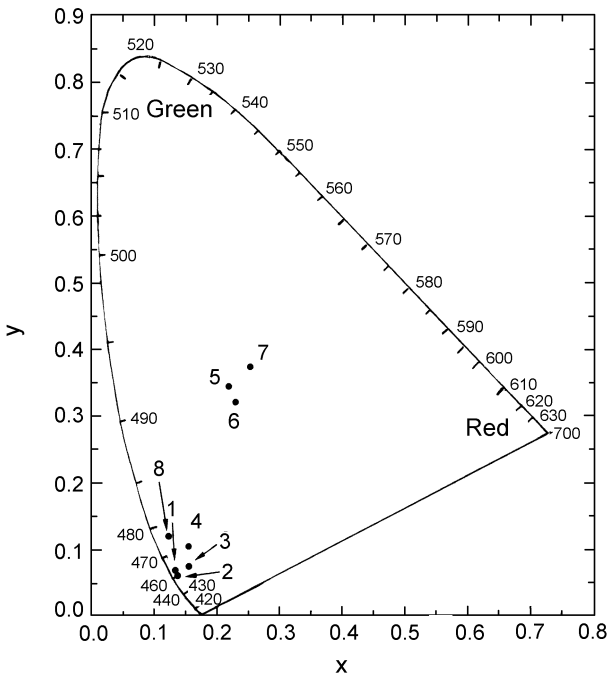


Figure 1. CIE Chromatocities diagram of chemiluminescent light of fluorophores **1-8**.

Optical properties. As expected for the conjugation length, the fluorophores were found to be pale yellow in color with an intense blue fluorescence. The UV-visible spectra of fluorophores are summarized in Table 2. There is a close resemblance between UV-vis spectra of the fluorophores. Fluorophores **3-7** showed a maximum absorption at 341-359 nm, while **1** and **2** displayed two well separated maxima between 260 and 335 nm, and 279 and 331 nm,

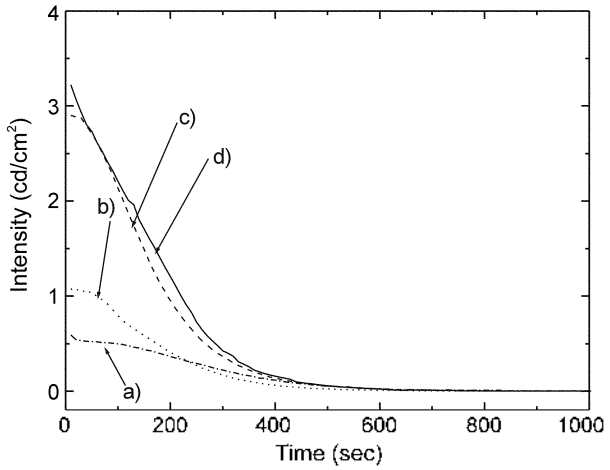


Figure 2. Decay of the chemiluminescent light intensity of a) **2**, b) **4**, c) **7** and d) **8**.

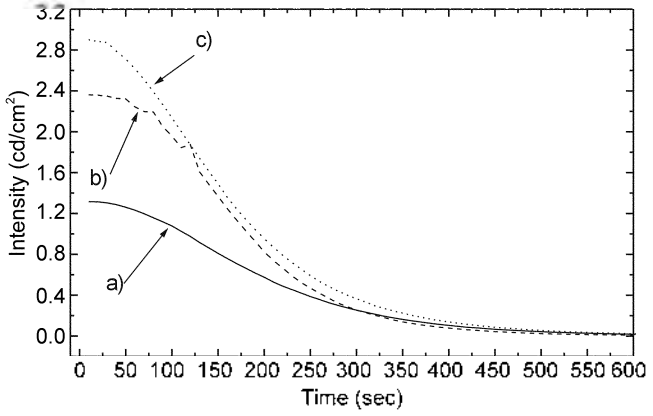


Figure 3. Decay of the chemiluminescent light intensity of a) **5**, b) **6** and c) **7**.

respectively. The two absorption bands at 260-295 and 335-359 nm were assigned to the naphthalene moiety and the conjugated biphenyl moieties, respectively. The absorption maxima of 4,4'-bis[2-(6-methoxynaphthyl)]biphenyl (**2**) was similar to those of 4,4'-bis(2-naphthyl)biphenyl without methoxy substitution.[21]

When the maximum absorption wavelength was irradiated, the fluorophores **1-7** displayed blue photoluminescence with maxima at 377-415 nm as listed in Table 2.

The emission spectra were dependent upon the chemical structure of fluorophores. The fluorene-containing fluorophore **4** showed a maximum at 382 nm, whereas 9,9-dibutyl-2,7-bis(2-naphthyl)fluorene without methoxy substitution showed it at 381 nm. Obviously the introduction of carbazole moiety instead of biphenyl group broadened the emission spectrum to longer wavelengths, which corresponds to electron donating effect of *N*-alkyl group of carbazole group. It is also apparent that the photoluminescent spectra of fluorophores **4** and **7** containing electron-donating methoxy group were shifted to longer wavelengths than those of 9,9-dibutyl-2,7-bis(2-naphthyl)fluorene and 9-butyl-3,6-di(1-naphthyl)carbazole.[21] The commercial blue fluorophore **8** tuned by the chloro- and methoxy-substituent showed a photoluminescent spectrum at 439 nm.

Chemiluminescence. An aliquot of the hydrogen peroxide and sodium salicylate catalyst solution was added into the solution of fluorophore and CPPO at 25 °C. After one minute, the two solutions were mixed completely, and the emission spectrum was scanned immediately. The fluorophore solution was activated instantly by the catalyst. The chemiluminescent spectra obtained from it were longer than normal photoluminescence spectra excited at their maximum absorption wavelengths. It was found that **4-7** were applicable to the chemiluminescent blue fluorophores, which are highly soluble in the dibutylphthalate system of the chemiluminescent reaction.

Chemiluminescent emission spectra of **1-7** appeared around 400 nm as shown in Table 2, while blue light emissions with shorter wavelengths have also been observed from them. The wavelengths of the emitted light are dependent upon the substituent as an auxochromophore as shown in Table 2.[22,23] In this experiment, we demonstrated that carbazole-containing fluorophores **5-7** showed peculiar sky blue emissions (λ_{max}= 420-427 nm) and that they were effective blue light-emitting fluorophores. Chemiluminescent emission intensities and color coordinates of fluorophores **1-7** in the CIE chromaticity diagram are shown in Figure 3 and Table 3. Comparing the CIE color coordinate, the color tones of blue light obtained from fluorophores **1-4** are similar to that of **8**, while **5-7** shifted to center of CIE color coordinate showing white blue light.

With regard to the practical use of the blue chemiluminescent fluorophore, it is worth studying their peroxide degradation. It is required that the fluorophore should be stable in the presence of hydrogen peroxide. The naphthalene containing biphenyl analogues have been known to be resistant to peroxide oxidative condition, therefore the fluorophores emitted a light with no change of CIE chromaticity value during chemiluminescent reaction.

A typical chemiluminescent decay curve for all the

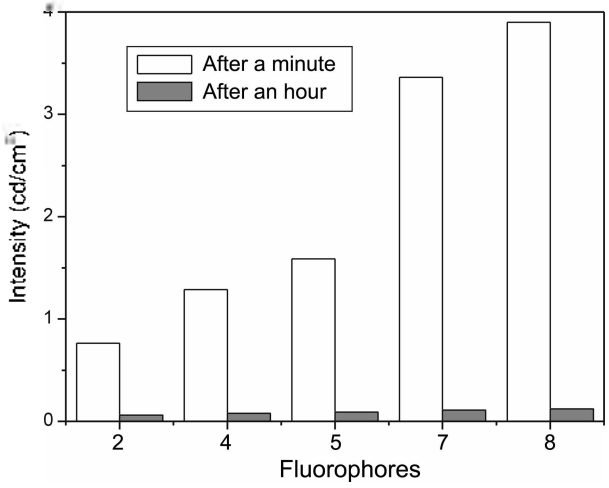


Figure 4. Comparison of light intensity of fluorophores with 2-chloro-9,10-di(*p*-methoxyphenyl)anthracene.

Table 3. Chemiluminescent intensity and color coordinate in the CIE chromaticity of naphthalene-containing biphenyl analogues

Fluoro-phores	Intensity (cd/cm^2)[a]		CIE Color Coordinate
	After 1 min	After 10 min	After 10 min
1	0.12	0.03	x = 0.14, y = 0.06
2	0.51	0.04	x = 0.14, y = 0.05
3	0.36	0.03	x = 0.14, y = 0.07
4	0.93	0.05	x = 0.15, y = 0.10
5	1.24	0.06	x = 0.22, y = 0.34
6	2.22	0.06	x = 0.24, y = 0.31
7	2.64	0.07	x = 0.25, y = 0.38
8	3.19	0.08	x = 0.12, y = 0.12

[a]Emitted intensity was obtained by using the concentrated catalyst solution.

fluorophores in DBP shows a rapid decay during the first 180 seconds followed by a much slower decay lasted over 40 min. The order of emitted intensity of fluorophores under same condition was **7** > **4** > **2** as shown in Figure 4 and **7** > **6** > **5** as shown in Figure 5. Much brighter chemiluminescent decay pattern was observed for the fluorophore **7**.

The fast decay of the chemiluminescent intensity may be due to the very fast reaction between CPPO and hydrogen peroxide. We speculate that the initial burst is controlled by changing the ratio of dimethylphthalate/*t*-butanol and concentration of sodium salicylate. These decay profiles can fit to exponential rate curve.

1-Naphthyl group and carbazole moiety in compound **5** form dihedral angle of 51°, while 2-naphthyl group and carbazole moiety in **6** changes dihedral angle from 4.39° to 33.23°. The dihedral angles between naphthyl and biphenyl group in **1** and **2** are quite different (49.14° for **1** and 1.38° for **2**). In the case of **1** the two aromatic rings form dihedral angle of 72.26°, whereas two aromatic rings in **2** exist in almost the same plane. It is found that a dihedral angle of 49° and 72° in **1** can diminish or even suppress the delocalization of π-electron and therefore limit the fluorescence.[23] It was found that the relationship between chemiluminescent emission intensity and dihedral angle is somewhat explained by comparing the data in Table 3 and Figures 3 and 4. The maximum brightness of chemiluminescence is ca.0.12-2.64 cd/cm^2 and 0.03-0.07 cd/cm^2 after 1 min and 10 min. respectively.

The comparisons of light intensity of a few fluorophores are shown in Figure 4. Chemiluminescent light obtained from **7** has a greater intensity than those of other dyes **2**, **4**, and **5** except a commercial fluorophore **8**. Chemiluminescent emission was maintained for more than 4 h and was visible with naked eyes.

In conclusion. various blue biphenyl analogues containing naphthalene moiety were prepared and applied for the chemiluminescent blue fluorophores. They were stable under peroxide oxidative conditions. and showed blue and sky blue through the chemiluminescent reaction. Chemiluminescent emission was maintained for more than 4 h and was visible with naked eyes.

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