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Chemiluminescent properties of blue fluorophores containing naphthalene unit

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Abstract

Various conjugated blue fluorophores containing naphthalene moiety in biphenyl analogues were synthesized via Suzuki reaction for the blue chemiluminescent fluorophore. UV–Vis absorption, photoluminescence and chemiluminescence were measured and evaluated. The fluorophores displayed blue photoluminescence in solution with maximum around 375–410 nm. Sodium salicylate-catalyzed reaction of hydrogen peroxide with bis(2-carbopentyloxy-3,5,6-trichlorophenyl) oxalate (CPPO) produced a strong chemiluminescent blue light emission with wavelengths of 398–420 nm in the presence of the fluorophores. The chemiluminescent intensity decayed exponentially and the glow of chemiluminescence maintained for more than 4 h and was visible with naked eye.

Keywords: 4,4′-Di(1-naphthyl)biphenyl; 9,9-Dibutyl-2,7-di(2-naphthyl)fluorene; 9-Butyl-3,6-di(2-naphthyl)carbazole; Blue fluorophore; Chemiluminescence

1. Introduction

Conventional chemiluminescent fluorophores are highly conjugated aromatic compounds such as *N,N'*-bis(2,6-diisopropylphenyl)-1,6,7,12-tetrakis(*p*-*tert*-butylphenoxy)-3,4,9,10-perylene tetracarboxydiimide, rubrene, 9,10-bis(*p*-methoxy-phenyl)-2-chloroanthracene and 9,10-bis(phenylethynyl)-2-chloroanthracene derivatives [1–5]. They are tailor-made for chemiluminescent fluorophores in consideration of chemical stability at oxidative condition and solubility in dibutylphthalate. A few examples appeared in the literature applying the blue fluorophores to chemiluminescent reaction. Appropriate substituents can tune the blue color and increase solubility and optical properties to meet the requirement for chemiluminescent fluorophores. Among the chemiluminescent fluorophores, especially blue fluorophores having anthracene moiety have been widely used in commercial and industrial applications because of the stability in peroxide oxidative conditions [6,7]. Recently, it was also reported that polymeric fluorophores containing 1,6,7,12-tetrakis(*p*-*t*-butylphenoxy)-3,4,9,10-perylene tetracarboxydiimide and 9,10-diphenylanthracene units were used as efficient violet color light-emitting chemiluminescent fluorophores [8–12].

In this report, various naphthalene-containing biphenyl analogues such as biphenyl, fluorene and carbazole were prepared and various optical

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properties including chemiluminescent characteristics were examined. They are a kind of blue fluorophores with deformations in geometric and chemical structure of molecules.

2. Experimental

2.1. Chemicals and instruments

2.1.1. Materials

4,4′-Dibromobiphenyl, 1-naphthaleneboronic acid, 6-methoxy-2-naphthaleneboronic acid and 2-naphthaleneboronic acid were purchased from Aldrich Chem. Co.. 2,7-Dibromo-9,9-dibutylfluorene and 9-butyl-3,6-dibromocarbazole were prepared by the method previously reported [13].

Potassium carbonate (Aldrich Chem. Co., 99.99%), sodium salicylate (Aldrich Chem. Co.), *t*-butanol, dibutyl phthalate (GR, Yakuri Co.) and dimethyl phthalate (GR, Junsei Chem. Co.) were used without further purification.

FT-IR spectra were obtained with a Midac Model M-1200 spectrophotometer and ^{1}H NMR spectra were recorded on a Varian Mercury plus spectrometer. Elemental analyses were performed using a Yanaco MT-3 CHN instrument. UV spectra were obtained on a Shimadzu model UV-2100S spectrophotometer. Intensity of the emission light was measured with a Minolta Chromameter CS-l00. Photoluminescence were measured on an Optical Spectra Multichannel Analyzer (OSMA-1000, Photodiodes 1024).

*2.1.2. 4,4′-Di(1-naphthyl)biphenyl (**1**)*

To a mixture of 4,4-dibromobiphenyl (1 g, 3.205 mmol) and 1-naphthaleneboronic acid (1.213 g, 7.051 mmol) in anhydrous THF (60 ml) and 70 ml of K_2CO_3 (1 M aqueous solution) was added anhydrous THF (30 ml) of $Pd(PPh_3)_4$ (0.163 g, 0.141 mmol) under nitrogen. 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 separation, the solvent in the organic layer was removed. Recrystallization was made in ethyl acetate. Similar experimental procedures were adopted for the preparation of fluorophores 4,4′-di(2-naphthyl)biphenyl (2).

*2.1.2.1. **1**. Yield: 53%.* Mp: 176–177 °C. FT-IR (KBr) 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. ^{1}H NMR ($CDCl_3$) δ 8.05–;7.48 (m, 22 H, aromatics). Anal. calcd for $C_{32}H_{25}$ (Mw, 409.552): C, 93.85; H, 6.15. Found:C, 93.76; H, 6.19.

*2.1.2.2. **2**. Yield: 42%.* Mp: 169–170 °C. FT-IR (KBr) 3035 (aromatic C–H). ^{13}C NMR ($CDCl_3$) δ 125.25, 125.64, 125.83, 125.92, 126.78, 127.55, 128.13, 130.39, 131.40, 133.641, 139.47, 139.62. ^{1}H NMR ($CDCl_3$) δ 7.43–8.16 (m, 22 H, aromatics). Anal. calcd for $C_{32}H_{25}$ (Mw, 409.552): C, 93.85; H, 6.15. Found: C, 93.79; H, 6.17.

*2.1.3. 9,9-Dibutyl-2,7-di(2-naphthyl)fluorene (**3**)*

Under nitrogen, to a mixture of 2,7-dibromo-9,9-dibutylfluorene (0.65 g, 1.498 mmol) and 2-naphthaleneboronic acid (0.567 g, 3.296 mmol) in anhydrous THF (30 ml) and 35 ml of K_2CO_3 (1M aqueous solution) was added anhydrous THF (15 ml) of $Pd(PPh_3)_4$ (0.076 g, 0.066 mmol). 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 separation, the solvent in the organic layer was removed. The residue was purified by a column chromatography (silica gel, hexane).

Similar experimental procedures were adopted for the preparation of fluorophore 9,9-dibutyl-2,7-bis[2-(6-methoxynaphthyl)]fluorene (**4**).

*2.1.3.1. **3**. Yield: 55%.* Mp: 180–181 °C. FT-IR (KBr) 3050 (aromatic C–H) 2960, 2840 (aliphatic C–H). ^{13}C NMR ($CDCl_3$) δ 14.08, 23.30, 26.26, 40.46, 55.37, 119.97, 121.59, 125.67, 126.13, 127.47, 127.97, 128.22, 132.354, 133.528, 138.75, 139.75, 139.91. ^{1}H NMR ($CDCl_3$) δ 7.45–8.10 (m, 20H, aromatics), 2.11 (t, 2H, C–CH_2–), 0.79 (m, 2H, C–CH_2–CH_2–), 1.19 (m, 2H, –CH_2 –CH_3), 0.70 (t, 3H, –CH_3). Anal. calcd for $C_{41}H_{38}$ (Mw, 530.755): C, 92.78; H, 7.22. Found: C, 93.06; H, 7.19.

*2.1.3.2. **4**. Yield: 34%*. Mp: 222–223 °C. FT-IR (KBr). 3058 (aromatic *C–H*), 2930, 2854 (aliphatic *C–H*), 1023 (ether *C–O*). ^{13}C NMR ($CDCl_3$) δ 14.06, 23.31, 29.85, 55.32, 55.41, 105.49, 119.00, 119.87, 125.29, 125.93, 127.05, 129.04, 129.48, 133.49, 136.61, 139.70, 139.75, 151.46, 157.40. ^{1}H NMR ($CDCl_3$) δ 7.14–8.06 (m, 18H, aromatics), 3.59 (s, 6H, methoxy), 2.05 (t, 2H, $C–CH_2$–), 0.79 (m, 2H, $C–CH_2–CH_2$–), 1.15 (m, 2H,–$CH_2–CH_3$), 0.70 (t, 3H, –CH_3). Anal calcd for $C_{43}H_{42}O_2$ (Mw, 558.809): C, 92.42; H, 7.58. Found: C, 92.36; H, 7.49.

*2.1.4. 9-Butyl-3,6-di(2-naphthyl)carbazole (**5**)*

Under nitrogen, to a mixture of 9-butyl-3,6-dibromocarbazole (0.65 g, 1.706 mmol) and 2-naphthaleneboronic acid (0.646 g, 3.753 mmol) in anhydrous THF (35 ml) and 40 ml of K_2CO_3 (1 M aqueous solution) was added anhydrous THF (20 ml) of $Pd(PPh_3)_4$ (0.087 g, 0.075 mmol). 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 separation, the solvent in the organic layer was removed. The residue was purified by a column chromatography (silica gel, 30% dichloromethane in hexane).

*2.1.4.1. **5**. Yield: 68%*. Mp: 160–161 °C. FT-IR (KBr) 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. ^{1}H NMR ($CDCl_3$) δ 7.18–8.57 (m, 20 H, aromatics), 3.87 (t, 2H, =$N–CH^2$–), 1.44 (m, 2H, $N–CH_2–CH_2$–), 0.72 (m, 2H, –$CH_2–CH_3$), 0.51 (t, 3H, –CH_3). Anal. calcd for $C_{36}H_{32}N$ (Mw, 478.659): C, 90.33; H, 6.74; N, 2.92. Found: C, 90.36; H, 6.49; N, 2.91.

2.2. Preparation of chemiluminescent solution

Blue fluorophore 4 (3×10^{-3} M) and bis(2-carbopentyloxy-3,5,6-trichlorophenyl) oxalate (CPPO, 3.90×10^{-3} M) were dissolved in dibutyl phthalate (20 ml) at 80 °C under nitrogen [14–18]. On the other hand, hydrogen peroxide (90%, 1.5 equivalent of CPPO) and sodium salicylate (2.5×10^{-5} M) were dissolved in 20 ml of mixed solvent of dimethyl phthalate/*t*-butanol (v/v, 4/1).

2.3. Measurements of chemiluminescence

Spectra of the chemiluminescence and the rates of catalytic decomposition of CPPO were obtained by conducting the reaction in a 1 cm square quartz cuvette in the sample compartment of spectrofluorometer. The cuvette was filled with hydrogen peroxide solution (0.6 ml) and the freshly prepared fluorophore solution (1.8 ml) was poured to mix instantaneously. Measurement of the signal was begun after one minute by opening the shutter and the chemiluminescent decay was generally recorded.

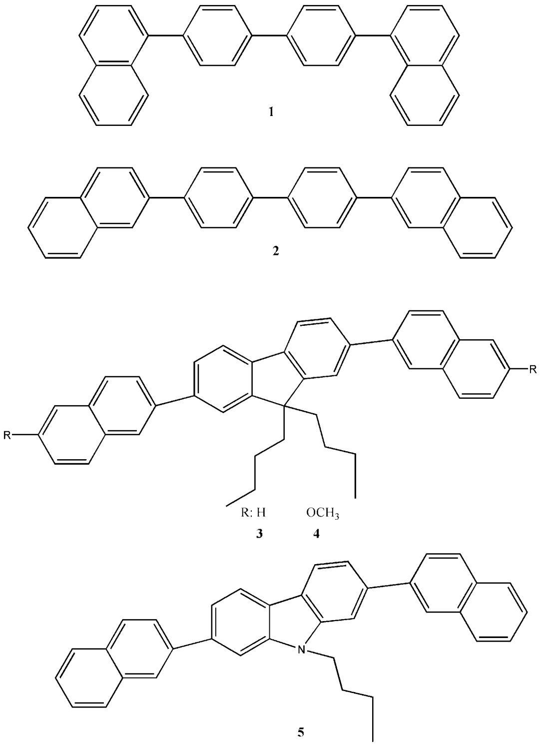
3. Results and discussion

3.1. Preparation and characterization of blue fluorophores

The Suzuki reactions [19–24], used to synthesize fluorophores containing naphthalene moiety in biphenyl analogues, were easily accomplished by the reaction of corresponding 4,4′-dibromobiphenyl, 2,7-dibromo-9,9-dibutylfluorene and 9-butyl-3,6-dibromocarbazole with various boric acid derivatives 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.

The fluorophores were characterized through the data from proton ^{1}H-NMR, ^{13}C-NMR, IR and elemental analyses. In the FT-IR spectra of the samples, bands were found in the 3030–3050 and 2950 cm^{-1} regions attributable to C–H stretching of the aromatic and aliphatic protons, respectively. In the ^{1}H NMR spectra, all samples showed aromatic protons at 7.1–8.5 ppm assignable to aromatic protons. On the other hand, multiplet peak at 0.76–2.02 ppm is attributed to the proton of butyl group of fluorene moiety and 3.6 ppm is attributed to the methylene proton of *N*-butyl group of carbazole. The CHN elemental



Scheme 1.

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

Fluorophores	Dihedral angle (degree)		Yield (%)
	Biphenyl analogue	Naphthyl and biphenyl analogue	
1	72.256	49.144/48.850	53
2	0.316	0.949/0.838	42
3	0	33.189/33.073	55
4	0	37.943/36.591	34
5	0	33.234/4.394	67

Table 2
The UV–Vis absorption, photoluminescent and chemiluminescent maximum wavelength of the naphthalene-containing biphenyl analogue

Fluorophores	UV (λ_{max})[a]	PL (λ_{max})[b]		CL
		abs (λ_{max})[d]	366 nm	(λ_{max})[c]
1	260/335	380	378	401
2	271/331	376	379	398
3	264/304/371	381/400	382/400	402
4	291/375	387/408	388/407	413
5	359	409	410	420

[a] Measured in chloroform solution.

[b] Measured in dibutyl phthalate solution.

[c] Measured during chemiluminescent reaction.

[d] Measured at the maximum absorption wavelength.

analysis values matched well with the data calculated from the expected chemical structure. Fluophores were soluble in common organic solvents such as chloroform, tetrahydrofuran and dibutyl phthalate.

In the literature, steric interactions between bulky groups may cause deformations of the geometric structure of a molecule. Of course, twisting of single bonds is by far the most important structure change. Thus in general steric strain in π system is relieved by rotation around formed single bond [25].

Certain structural characteristics of biphenyl analogues were determined by means of the CS Chem3D Pro v. 5.0 modeling system. Table 1 presents the optimized geometries of biphenyl analogues, which were obtained after energy minimization. The calculations were carried out with full geometry optimization (bond length, bond angle and dihedral angle). It seems that **1** deviated significantly from the coplanar conformation. Particularly, all naphthyl groups formed with the adjacent biphenyl group dihedral angles range from 1 to 49°. The twist angle between the biphenyl groups and the adjacent naphthyl was 49° and 1° for compound **1** and **2**, respectively.

3.2. Optical properties

The UV absorbance, photoluminescence as well as the chemiluminescent characteristics of naphthalene-containing biphenyl analogue fluorophores **1–5** were measured and listed in Table 2.

In Fig. 1, the λ_{max} values of **1–5** are as follows: 335 nm for **1**, 331 nm for **2**, 371 and 375 nm for **3–4**, and 359 nm for **5**. From the results, it is apparent that fluorophore **4** having electron-donating groups (–OMe) show a bathochromic shift. Additionally, shapes of curves **1** and **2** are similar to one another but different from curve **3**,

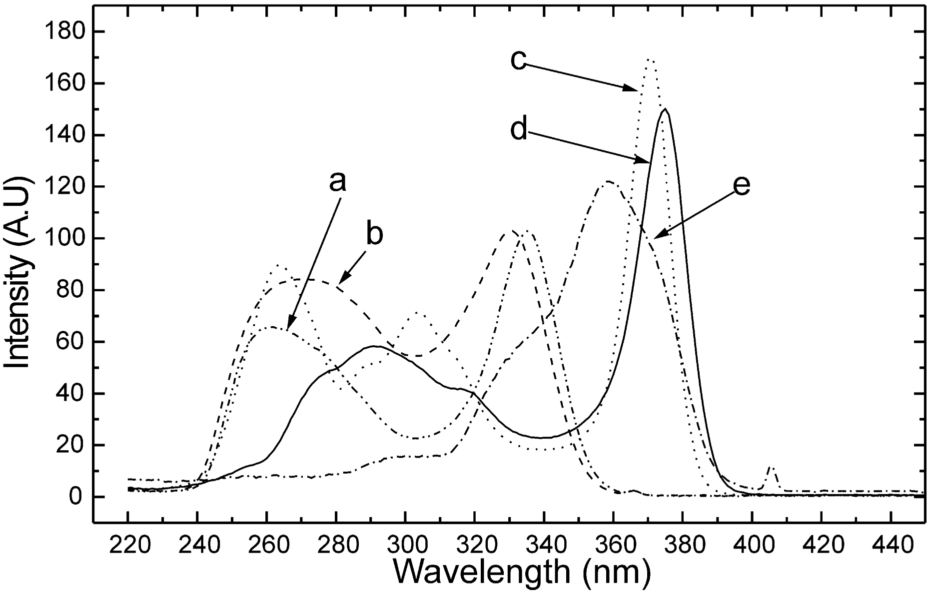


Fig. 1. UV–Vis absorption spectra of (a) **1**, (b) **2**, (c) **3**, (d) **4** and (e) **5** in concentration of 3×10^{-5} mol.

4 and **5**. The maximum absorption and emission of these fluorophore changed with the chemical structure, for example the absorption maximum for the fluorophore **2** with 2-naphthyl moiety appeared at 331 nm and blue-shifted by 4 nm compared with **1** with 1-naphtyl group.

It can be attributed to the torsional angle between naphthalene and the biphenyl moiety in compound **1** changes from 1° to 49° and in 2 from 0° to 0.9°.

Compared with these fluorophores, the absorption and emission spectra of **3** and **4** are red-shifted, because the incorporation of dialkyl groups at 9-position make the biphenyl ring rigid.

The results of the investigation of photoluminescence for **1–5** are presented in the Fig. 2. The photoluminescence spectra were obtained by irradiating light with their maximum absorption wavelength (Fig. 2) or at wavelength of 366 nm (Fig. 3). The fluorophores displayed blue photoluminescence in solution with maxima around 375–410 nm.

3.3. Chemiluminescence

An aliquot of the hydrogen peroxide and sodium salicylate catalyst solution was added into the solution of fluorophore and CPPO at 25 °C. It was found that the fluorophore **1–5** were highly efficient blue fluorophores, which are highly soluble in the dibutyl phthalate system of the chemiluminescent reaction. After one minute the two components were mixed completely, and the emission spectrum was immediately scanned. The fluorophore solution is activated instantly by the catalyst solution. The results of chemiluminescent spectra obtained were longer than normal photoluminescence spectra excited at their maximum absorption wavelengths. Chemiluminescent emission spectra of **1–5** appeared around 400 nm as shown in Table 2. Typical blue light emissions have been observed from them. The wavelengths of the emitted light are dependent on the substituent as an auxochromophore in the fluorophore. Fluorophore **4** showed blue emission ($\lambda_{max} = 413$ nm). In this experiment, fluorene-containing fluorophores were efficient blue light-emitting fluorophores. Table 3 also shows chemiluminescent emission intensity and color coordinate of fluorophore **1–5** in the CIE chromaticity diagram as shown in Table 3.

With regard to the practical usage of the blue chemiluminescent fluorophore, it is worth studying their peroxide degradation. It is required that

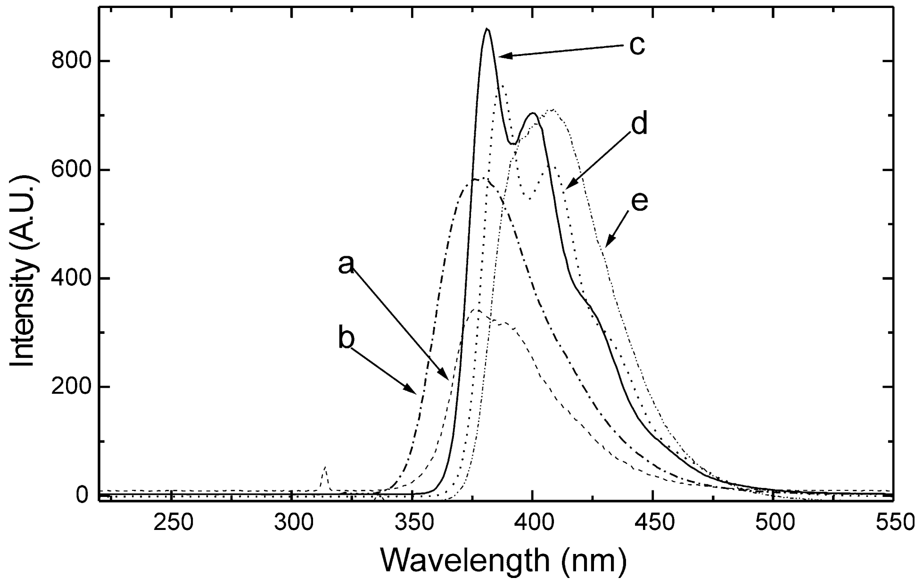


Fig. 2. Photoluminescent spectra of (a) **1**, (b) **2**, (c) **3**, (d) **4** and (e) **5** at their maximum absoption wavelength.

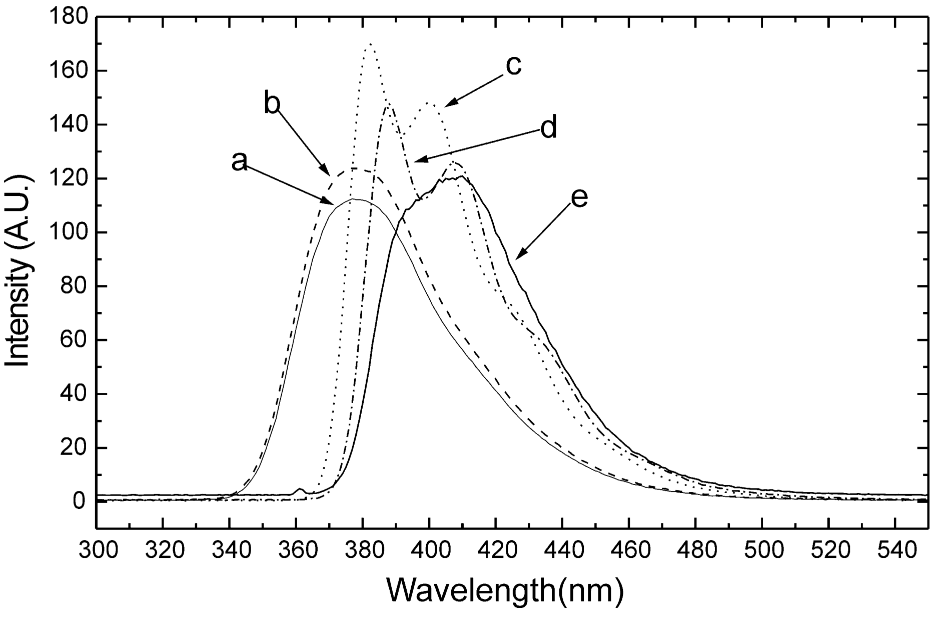


Fig. 3. Photoluminescent spectra of (a) **1**, (b) **2**, (c) **3**, (d) **4** and (e) **5** at 366 nm wavelength.

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 conditions, but the fluorophores emitted a light with no change of CIE chromaticity value during chemiluminescent reaction.

A typical chemiluminescent decay curve for all the fluorophores in DBP shows a rapid decay during the first 45 minutes followed by a much

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

Fluorophores	Intensity (cd/cm^2)		CIE color coordinate
	After 12 min	After 1 h	After 10 min
1	0.89	0.14	$x = 0.1350$, $y = 0.0597$
2	1.47	0.23	$x = 0.1361$, $y = 0.0489$
3	2.72	0.51	$x = 0.1448$, $y = 0.0563$
4	3.05	0.55	$x = 0.1534$, $y = 0.1005$
5	4.92	0.89	$x = 0.2380$, $y = 0.3138$

slower decay lasting over 4 h. A similar, but much brighter chemiluminescent decay pattern was observed for the fluorophore **5**.

The very fast decay of the chemiluminescent intensity may be explained as due to the very fast reaction between CPPO and hydrogen peroxide, owing to the very high surface in the heterogeneous solvent system. We speculate that the initial rapid reaction is controlled by the component of solvents, therefore we used dimethylphthalate/*t*-butanol (v/v, 4/1) as a catalyst solvent [15–18]. These decay profiles can be fitted to exponential rate curve.

The relationship between the quantum yield of the fluorescence and molecular structure is determined to a large extent by the structural dependence of the competing photophysical and photochemical processes. Thus for most rigid aromatic compounds fluorescence is easy to observe, with quantum yields in the range $1 > \Phi_F > 0.01$. For example, it is well known that in 1 a twist angle greater than 49° and 72° can diminish or even suppress the conjugation and therefore limit the fluorescence [25]. Chemiluminescent properties is closely related with the molecular structure of fluorophores.

The decay intensities of the chemiluminescence for the blue fluorophores are shown in Fig. 4. Chemiluminescent emission was maintained for more than 4 h and was visible with naked eye. The maximum brightness of CL is ca.0.89–4.92 cd/cm^2 and 0.14–0.89 cd/cm^2 after 12 min and after 1 h, respectively.

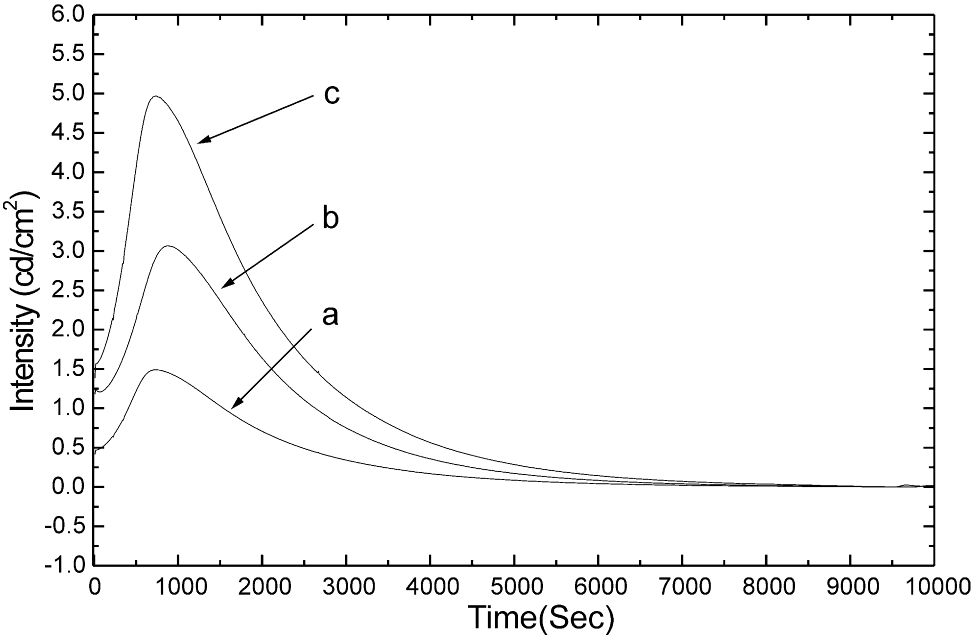


Fig. 4. Decay of the chemiluminescent light intensity of (a) **2**, (b) **4** and (c) **5**.

4. Conclusion

Various blue chemiluminescent biphenyl analogue fluorophores containing naphthalene moiety were stable under peroxide oxidative condition whereas they showed a moderate decay time of which profiles fitted to exponential rate curve. They were applicable to the commercial blue fluorophore for the chemiluminescence. The color of fluorophores can be maintained from blue to sky blue through the chemiluminescent reaction.

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