

# Sol–gel derived dye-bridged hybrid materials for white luminescence

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**Abstract** Novel yellow and blue emissive dyes have been synthesized using 2,5-diamino-3,6-dicyanopyrazine and various alkoxy silanes and they are covalently bridged to cycloaliphatic epoxy functional oligosiloxane via non-hydrolytic sol–gel reaction. Dye-bridged hybrid materials (DBH) are fabricated by thermal curing the dye-bridged oligosiloxane. Structure and formation of dyes and siloxane network is studied using analysis method. Four components of red, yellow, green and blue emitting DBH cover entire visible range and white luminescence with high color rendering index is realized by controlling their combinations. We have ensured superior thermal stability DBH at 120 °C for 200 h caused by covalently bridged structure and robust siloxane matrix.

**Keywords** Sol–gel · Hybrid material · Covalently bridged dye · White luminescence

## 1 Introduction

There have been many efforts to produce of full-color emission and white luminescence since they have an important role in full-color display and lighting technology. White luminescence is composed of red, green and blue

components or yellow and blue combination. Thus, it is necessary to fabricate full-color emitting material which covers whole visible range of 400–750 nm. Light emitting diode [1, 2], inorganic phosphor [3–5], rare earth complex [6, 7], conducting polymer [8], quantum dot [9, 10], organic dye [11] and their combinations are investigated as primary color emitter to generate white luminescence. Among these, dye has merit on cost and optical properties to be used as luminescent material. Absorption band of the dye is broad to have high efficiency and it is easy to modify the structure to generate various luminescence. But it has disadvantage on stability because it degrades by oxygen, moisture, heat and external light.

Recently, we have reported dye-bridged hybrid materials (DBH) [12, 13] which are one-body system of dye and matrix consisted with sol–gel derived oligosiloxane to overcome the limitation of the dye usage. In DBH, dyes are chemically bridged to oligosiloxane, thereby dyes are seized and caged by the dense siloxane network and it leads more stable characteristics. Molecular stacking of dye molecule is prevented by the covalently bridged structure, so the concentration stability is enhanced and high dispersion of dye in matrix was obtained. We have demonstrated that photoluminescence characteristic was not diminished under 120 °C heat for hundreds hours. Also, photoluminescence intensity of DBH has less sensitivity to temperature to preserve initial characteristic on elevated temperature because internal molecular rotation is restricted by the chemical structure. And it has good processability to be used as not only coating material but also solid bulk samples. DBH can be applied to dye laser material and luminescence converter of white LED.

In this study, novel yellow and blue emitting DBH have been synthesized on the base of epoxy functional oligosiloxane. 2,5-Diamino-3,6-dicyanopyrazine [14] is used

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as core substance for dye molecule and it is modified to emit different colors by bridging various alkoxysilanes. Here we report detailed studies on synthesis of DBH via non-hydrolytic sol–gel reaction and structure analysis. Photoluminescence characteristics are analyzed and white luminescence is realized by mixing the full-color emitting DBH under UV irradiation. Also, long term thermal stability at 120 °C for 200 h is measured to prove the potential of stable white emitting source.

## 2 Experimental section

### 2.1 Synthesis of dye-bridged alkoxysilanes (DBA)

The red and green emitting DBAs are synthesized by following the same method of references [12, 13]. For synthesis of yellow emitting DBA (Y-DBA), 2,5-diamino-3,6-dicyanopyrazine (DADCP, 4.0 mmol) and (3-aminopropyl)trimethoxysilane (APTS, 8.0 mmol) mixture were stirred at 70 °C for 12 h. The cyano group of DADCP and the amino group of APTS was reacted for amidine formation. Then 16.5 mmol of cyclohexanone was added to the mixture and stirred for 2 h at room temperature. After reaction, residual cyclohexanone was evaporated at 70 °C under vacuum condition. Both DADCP (4.0 mmol) and 3-(triethoxysilyl)propyl isocyanate (IPTES, 8.0 mmol) were used to synthesize the blue emitting DBA (B-DBA). They were stirred at 80 °C for 4 h using sodium hydroxide as catalyst to promote the formation of pyrimidine ring as a result of reaction between neighboring amino and cyano groups of DADCP and isocyanate of IPTES.

### 2.2 Synthesis of dye-bridged oligosiloxanes (DBO) and dye-bridged hybrid materials (DBH)

DBO was synthesized using the DBA, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (ECTS, 0.108 mol), and diphenylsilanediol (DPSD, 0.075 mol) via non-hydrolytic sol–gel reaction. The DBA and ECTS were mixed and stirred for 1 h with barium hydroxide monohydrate as a catalyst. The amount of the barium hydroxide monohydrate was 0.2 mol% of total precursors (DBA, ECTS and DPSD). And the amount of DBA was controlled to have 0.1 mmol L<sup>-1</sup>–5 mmol L<sup>-1</sup> of dye concentration in the DBO. The DPSD (0.015 mol) was added for 5 times for every 10 min to this solution and the mixture was reacted for 4 h at 80 °C to complete the formation of oligosiloxane. Alcohol, byproduct of sol–gel reaction, was removed by nitrogen purging during the reaction. The synthesized DBO was filtered with a 0.45 µm-diameter Teflon filter to remove solid catalyst. To make solid-state DBH sample, hexahydro-4-methylphthalic anhydride and

tetrabutylphosphonium methanesulfonate were used as hardener and initiator, respectively. The equivalent molar ratio of DBO and hardener was 1.0 : 0.9 and the amount of initiator was 1 mol% of DBO. DBO was thermally cured at 150 °C for 2 h and finally DBH was fabricated. The synthesis scheme of the DBA to DBH is represented in Scheme 1.

### 2.3 Characterization

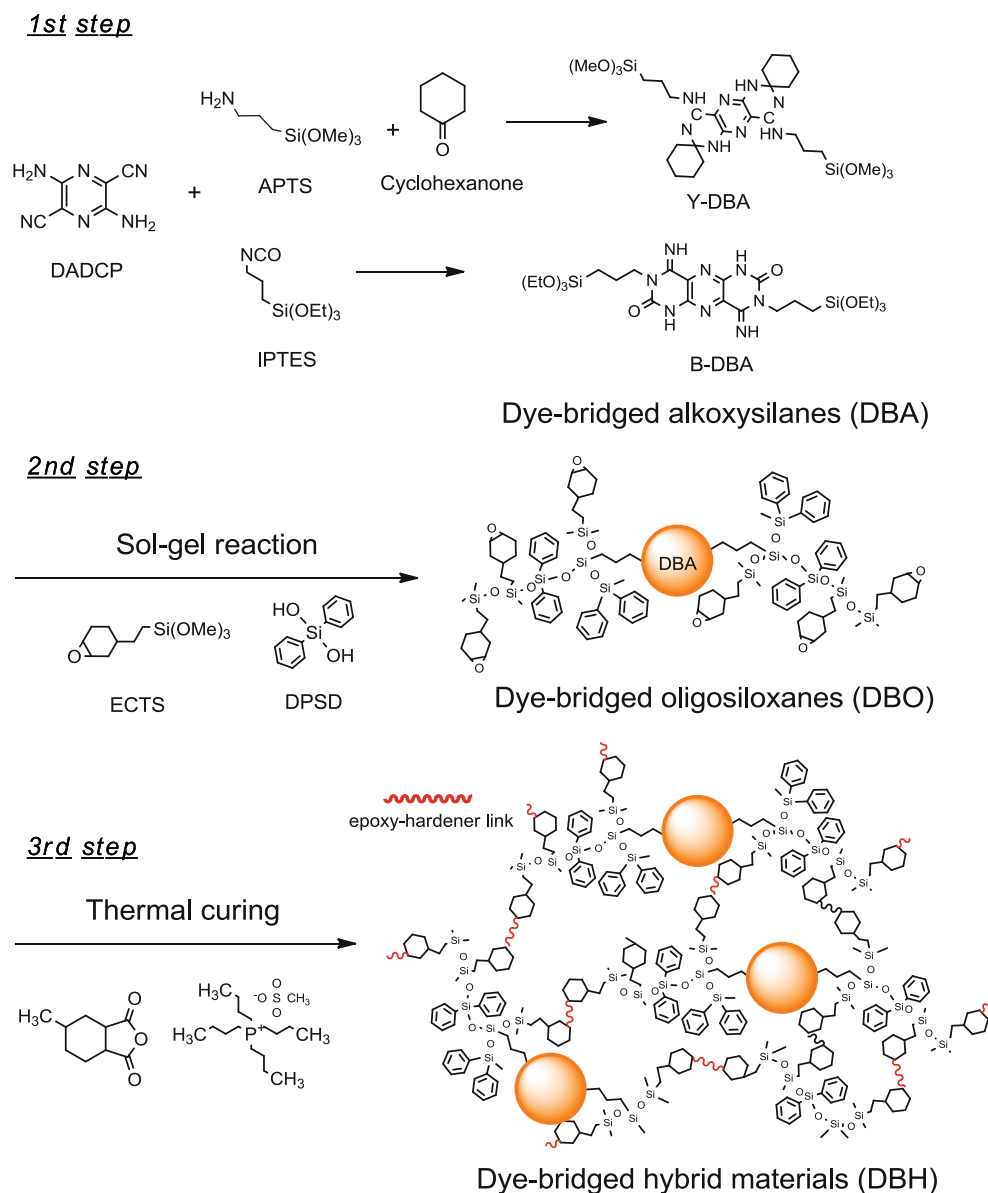
Fourier transform infrared (FT-IR) spectra were measured using FT-IR 680plus instrument (Jasco). Scanning resolution was 4 cm<sup>-1</sup> in the wavenumber range 650–4,000 cm<sup>-1</sup>. Formation of DBA and DBO was confirmed using FT-IR. <sup>29</sup>Si-NMR analysis was performed using 600 MHz NMR spectrometer (DMX 600, Bruker). For the <sup>29</sup>Si-NMR analysis, DBO was dissolved in CDCl<sub>3</sub> with chromium(III) acetylacetonate as a relaxation agent of silicon. Molecular weight distribution of DBO was examined by matrix-assisted laser desorption and ionization time-of-flight mass spectrometry (MALDI-TOF MS). MALDI-TOF MS spectra were evaluated with a Voyager DE-STR, 4700 proteomics analyzer. For the measurement, 2,5-dihydroxybenzoic acid and acetone were used as matrix and solvent of DBO, respectively. The thermal stability of polymerized DBH was confirmed using thermogravimetric analyzer (TGA, TA instrument) with a heating rate of 5 °C per minute under nitrogen atmosphere. Photoluminescence characteristics were measured by DARSA PRO 5100 PL spectrometer (Professional Scientific Instrument Co., Korea) using a Xe lamp as an excitation source at room temperature.

## 3 Results and discussion

### 3.1 Structure analysis of dye-bridged alkoxysilanes (DBA)

DBA is synthesized by covalent bridging of dye and alkoxysilane and the FT-IR spectra analysis verifies the structural formation as shown in Fig. 1. For Y-DBA, the cyano group of DADCP at 2,232 cm<sup>-1</sup> disappears and the C=NH band and amino group of amidine are seen at 1,634 cm<sup>-1</sup> and 1,600 cm<sup>-1</sup>, respectively, when DADCP and APTS are bridged. After cyclohexanone reacted, above amidine related bands and carbonyl peak of cyclohexanone at 1,705 cm<sup>-1</sup> are disappeared and new C=N stretching band result of amine/ketone reaction at 1,656 cm<sup>-1</sup>. For B-DBA, the isocyanate group of IPTES at 2,265 cm<sup>-1</sup> and the cyano group of DADCP at 2,232 cm<sup>-1</sup> does not appear after reaction at 80 °C for 4 h. Instead, strong peak of C=O at 1,700 cm<sup>-1</sup> are arisen and broad band around 3,335 cm<sup>-1</sup> of

**Scheme 1** Synthesis scheme of dye-bridged alkoxy-silanes (DBA) to dye-bridged hybrid materials (DBH) via sol-gel process



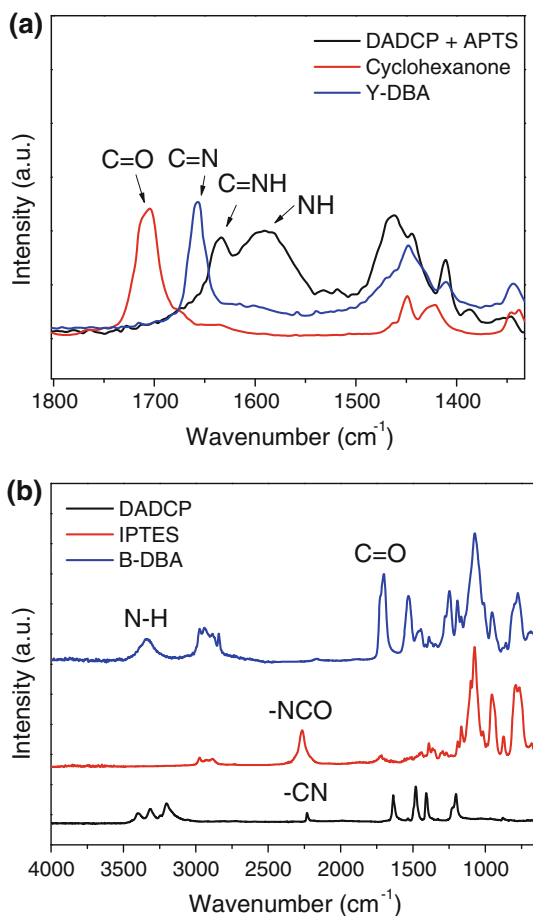
N–H stretching are appeared. These are pyrimidine ring related bands. From FT-IR analysis result, it can be concluded that DADCP dyes are covalently bridged to various alkoxy-silane and the DBA is successfully synthesized.

### 3.2 Formation of dye-bridged oligosiloxanes (DBO)

The formation of siloxane bond of DBO has been analyzed through FT-IR spectra analysis with time interval of 1 h (Fig. 2). DBO has been synthesized via non-hydrolytic sol-gel reaction using precursors of DBA, ECTS and DPSD. Absorption band of epoxy groups appears at  $883\text{ cm}^{-1}$ , which are the cross-linking moieties to fabricate DBH through polymerization. Absorption band of siloxane bond gradually increases in the range of  $1,000\text{--}1,150\text{ cm}^{-1}$  as

the sol-gel reaction proceeds. And the broad band intensity of hydroxyl group at  $3,200\text{--}3,600\text{ cm}^{-1}$  has been reduced because hydroxyl groups of DPSD react with alkoxy groups of organo-alkoxy-silanes to form siloxane bonds during sol-gel process. Absorption spectra of siloxane band and hydroxyl group are not changed after 4 h reaction and the siloxane formation is complete.

With  $^{29}\text{Si}$ -NMR measurement, the formation of siloxane bond of DBO is also confirmed (Fig. 3). Different oxygen bridging of the Si atoms can be identified through chemical shifts. DBA and ECTS are trimeric species which are denoted as  $T^n$ , where the superscript 'n' represents the number of siloxane bonds of the Si atoms, and DPSD is dimeric species denoted as  $D^n$ .  $T^0$  species of DBA and ECTS and  $D^0$  species of DPSD are not detected in



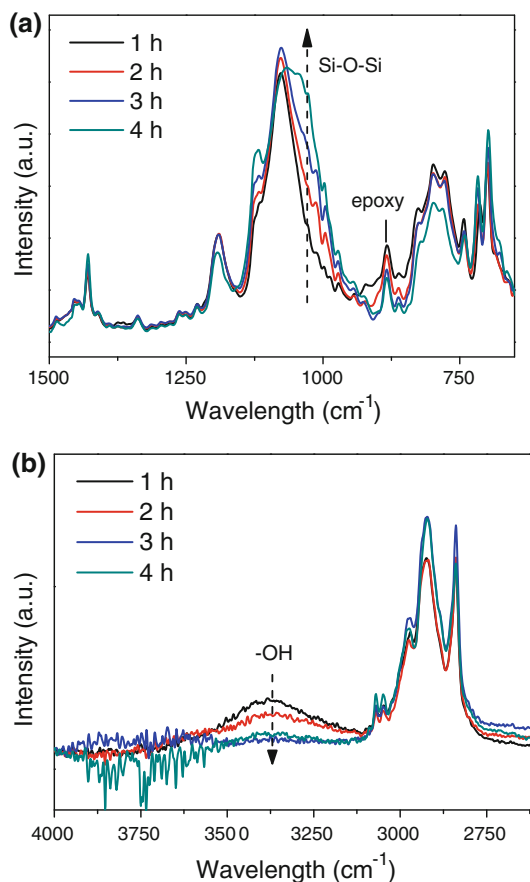
**Fig. 1** FT-IR spectra of the **a** precursor mixture of DADCP, APTS and cyclohexanone before reaction and result of Y-DBA after reaction, and **b** DADCP and IPTES before reaction and reaction result of B-DBA

<sup>29</sup>Si-NMR spectra that there are no unreacted monomers in DBO which represents the siloxane network is well formed. The degree of condensation (DOC) of the DBO is 71% that DOC is calculated with the peak area of <sup>29</sup>Si-NMR by the following equation.

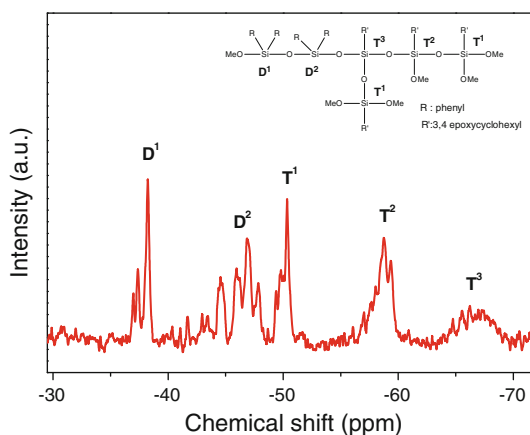
$$DOC = \frac{D^1 + 2D^2 + T^1 + 2T^2 + 3T^3}{2(D^0 + D^1 + D^2) + 3(E^0 + E^1 + T^2 + T^3)} \times 100 \quad (1)$$

### 3.3 Photoluminescence of dye-bridged hybrid materials (DBH)

DBH is fabricated by thermal curing of DBO and the photoluminescence spectra of the DBH are measured as shown in Fig. 4a. R-DBH, Y-DBH, G-DBH and B-DBH have main emission peaks at 660, 567, 525 and 443 nm, respectively. They represent various colors depending on the dye contents and the dye concentration is fixed to have 1 mmol L<sup>-1</sup>. The color coordinates of the DBH are pointed on Commission Internationale de l’Eclairage (CIE) 1,931 color space

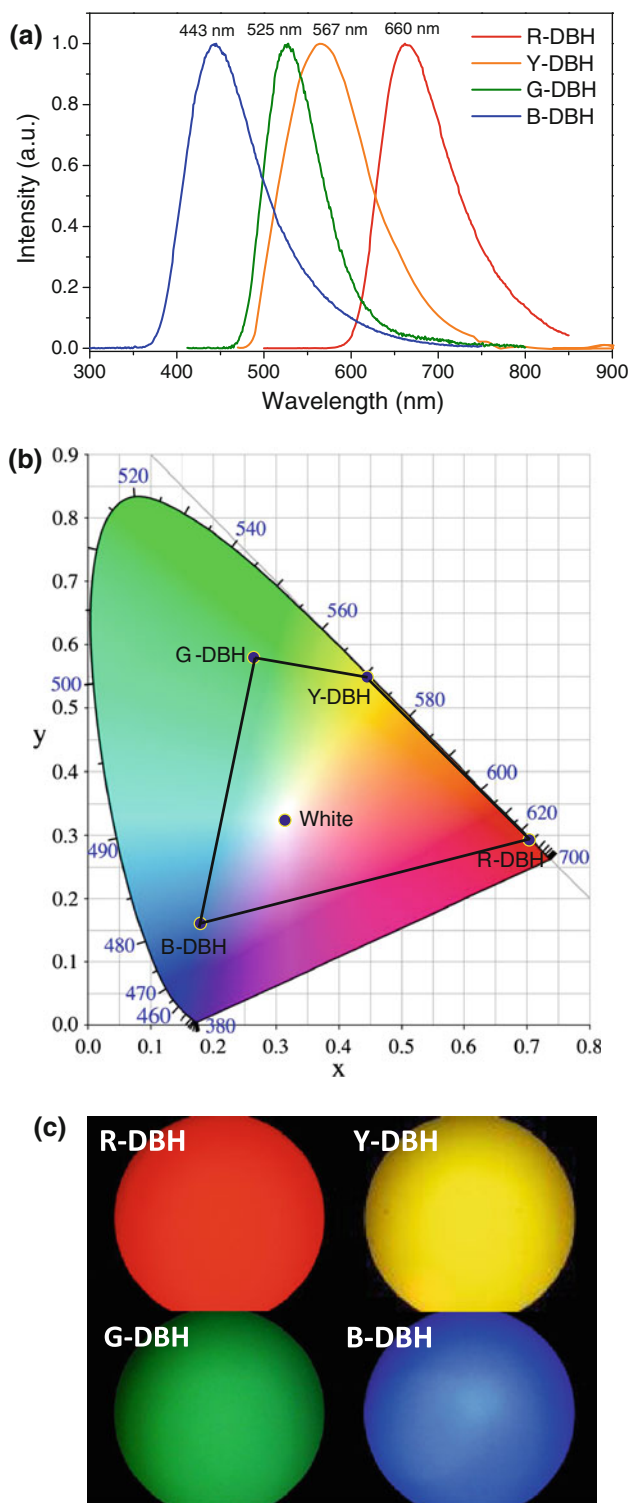


**Fig. 2** FT-IR spectra of DBO in the range of **a** 700–1,500 cm<sup>-1</sup> and **b** 2,600–4,000 cm<sup>-1</sup>. As the non-hydrolytic sol-gel reaction proceeds, the absorption band of siloxane bond increases and that of hydroxyl group decreases



**Fig. 3** <sup>29</sup>Si-NMR spectra of DBO. *Inset* Dimeric and trimeric species of siloxane bonding structure

(Fig. 4b). Each DBH has color coordinates of (0.705, 0.292), (0.446, 0.549), (0.265, 0.58) and (0.180, 0.160) in the color space, in the order of R-, Y-, G- and B-DBH. The full-color photoluminescence of DBH, photographs of the samples are



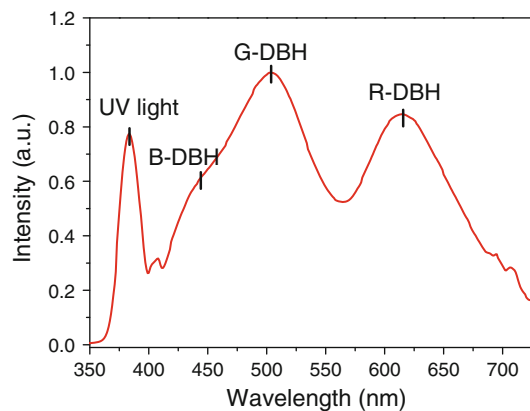
**Fig. 4** **a** Normalized photoluminescence spectra of R-, Y-, G- and B-DBH. They have main emission peaks at 660, 567, 525 and 443 nm, respectively. **b** Commission Internationale de l'Éclairage (CIE) color coordinates of the DBHs and white luminescence based on DBH mixture excited by UV lamp. **c** Photographs of the full-color photoluminescence of DBH under UV irradiation

represented in Fig. 4c. UV lamp was used as an excitation source and the photographs were taken using microscope. It is clearly observed DBH exhibits distinct bright full-color emission.

By adjusting the RGB luminescent, white luminescence is obtained from DBH mixture (Fig. 5). R-, G- and B-DBH was mixed with weight ratio of 1:6:4 and the dye concentration of R-DBH is  $1 \text{ mmol L}^{-1}$  and that of G-DBH and B-DBH are  $5 \text{ mmol L}^{-1}$ . Less amount of R-DBH is required compare to other components to make white luminescence because absorption spectrum of R-DBH is in the range of emission spectra of G-DBH and B-DBH and energy transfer occurs from G-DBH and B-DBH to R-DBH. From white luminescence, each color spectrum is overlapped due to their broad emission spectra. Especially, green and blue spectra are closely packed because difference of main emission between two components is relatively low to 80 nm. A white luminescent DBH has color coordinate of (0.315, 0.323), which is close to the theoretical white of (0.333, 0.333), and the color temperature is 6,459 K, and the color rendering index is 81. UV lamp was used as an excitation source for the white luminescence. It is known that color rendering index of fluorescent lamp for room illumination is about 70–80. Thus, the white luminescent DBH has comparable performance to be used as an illumination element.

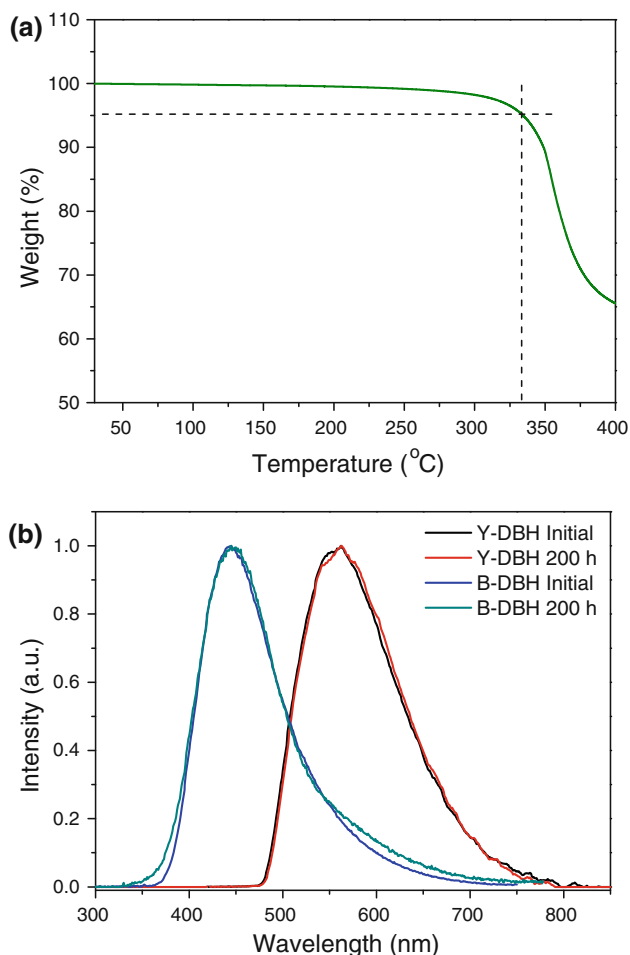
### 3.4 Thermal stability of dye-bridged hybrid materials (DBH)

In general, illumination sources such as LED or UV lamp generate lots of heat, thus, thermal stability is an important factor for illumination element to have permanent performance. Figure 6a shows a TGA analysis of DBH to confirm



**Fig. 5** Normalized white luminescence spectra obtained from R-, G- and B-DBH mixture under UV excitation source





**Fig. 6** **a** TGA analysis of DBH. The 5% weight loss temperature is 334 °C is indicated by *dashed line*. **b** Photoluminescence intensity of Y-DBH and B-DBH before and after thermal aging at 120 °C for 200 h in the air atmosphere to ensure the temporal and thermal stability

the thermal stability. The 5% weight loss temperature of DBH is 334 °C as shown in the TGA curve.

The photoluminescence intensity depending on thermal aging has been measured at 120 °C for 200 h in the air atmosphere to ensure the temporal and thermal stability (Fig. 6b). The photoluminescence intensity and main emission peak of Y-DBH and B-DBH is maintained the initial state after 200 h, which means dye molecules are not degraded under heating condition. It is considered that high temporal and thermal stability of DBH is because inorganic siloxane network and covalent bridged structure of DBH immobilize and protect the dye molecules.

## 4 Conclusion

Full-color emitting hybrid materials with covalently bridged dye have been synthesized. Especially, novel yellow and blue emitting hybrid materials are demonstrated in this report. We have confirmed that oligomer size siloxane structures are well formed in dye-bridged oligosiloxane via non-hydrolytic sol-gel reaction. In particular, white luminescence is obtained by controlling the ratio of RGB components using UV light source. It has good color rendering index of 81 to be used as an illumination source. Robust matrix consisted with siloxane network and covalently bridged structure lead the high thermal stability of dye molecules not to change the photoluminescence characteristics at 120 °C for 200 h. We expect dye-bridged hybrid materials will provide a promising strategy to develop full-color display and white lighting technology.

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