Anisotropic Polysilsesquioxanes with Fluorescent Organic Bridges: Transcription of Strong $\pi-\pi$ Interactions of Organic Bridges to the Long-Range Ordering of Silsesquioxanes

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A novel type of fluorescent and anisotropic polysilsesquioxane xerogel (**CNPBESi**) was synthesized by the acid-catalyzed classical sol−gel reaction of organically modified silicates. Anisotropy and enhanced fluorescence emission were simultaneously induced by the strong self-assembly power of the organic bridge units. **CNPBESi** was found to have a long-range order within the xerogel structure by X-ray diffraction analysis. Bright bluish green fluorescence emission from **CNPBESi** was attributed to the aggregation-induced enhanced emission of the organic bridge structure.

Introduction

Silicon-based organic−inorganic hybrid materials prepared by the sol−gel process are able to retain anisotropic properties with short- to long-range order if the chemical reactivity and molecular structure of the organic components are properly designed.[1,2] Since the first report on self-organized organic−inorganic hybrid materials prepared using polysilsesquioxanes,[3−8] many researchers have focused on developing novel functional materials by carefully designing the molecular architecture of the organically bridged poly(trimethoxysilylated) precursor. By tuning the precursor structure at the molecular level, researchers have prepared various highly structured materials, including a xerogel with high anisotropicity prepared by solid-state condensation,[6,9] an anisotropic xerogel obtained from a precursor with a mesogen-like organic bridge,[10,11] and a lamellar structured xerogel whose structure is induced by H-bond self-assembly of a urea or amide moiety in the organic bridge.[12−14] By using an optically or electronically active moiety as the organic bridge, exceptionally high contents of the active moiety could be introduced and homogeneously distributed in the mechanically robust hybrid material. These hybrid materials can be used in device applications such as waveguides,[15] light-emitting diodes,[16] and nonlinear optical devices.[17]

To produce self-organized anisotropic xerogels with fluorescent characteristics, Moreau and co-workers[18] and Corriu et al.[19] prepared xerogels from bridged silsesquioxanes containing phenylene-vinylene type organic bridges. Unfortunately, these xerogels exhibited neither strong fluorescence nor anisotropy, most likely due to significant concentration quenching and insufficient self-assembly of the fluorescent bridge units, respectively. Because both concentration quenching and anisotropy are commonly attributed to the self-assembly of bridge units, attempts to prepare strongly fluorescent anisotropic polysilsesquioxanes have been unsuccessful to date. Herein, we present a new strategy for simultaneously obtaining anisotropy and strong fluorescence by using the very unconventional fluorescent bridge unit free from concentration quenching but retaining strong self-assembly. This unconventional class of fluorescent molecules is characterized by aggregation-induced enhanced emission (AIEE) and is based on 1-cyano-1,2-bisbiphenyl-ethylene

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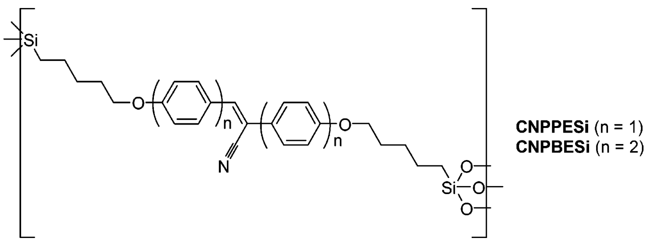
Scheme 1. Structures of the Xerogels



derivatives (**CNMBE** and **CNTFMBE**).[20,21] These fluorophores have strong $\pi-\pi$ interactions between rigid rodlike aromatic segments, allowing the easy transformation of the molecules into nanowires or stable nanoparticle suspensions that exhibit strong fluorescence. Recently, we demonstrated that the intermolecular $\pi-\pi$ interaction of the **CNMBE** moiety was strong enough to prepare densely packed self-assembled monolayers on oxidized silicon substrates.[22] In this study, we synthesized a novel fluorescent silsesquioxane derivative containing 1-cyano-1,2-bisbiphenyl-ethylene moiety (Scheme 1) as an organic bridge. Using this novel derivative, we obtained highly fluorescent anisotropic xerogels through the strong intermolecular $\pi-\pi$ interactions and enhanced fluorescence emission from the 1-cyano-1,2-bisbiphenyl-ethylene moiety.

Experimental Section

Materials. 4-Hydroxybenzaldehyde, 18-crown-6-ether, 5-bromo-1-pentene, 4-bromo-benzaldehyde, (4-hydroxy-phenyl)-acetonitrile, and tetrabutylammonium hydroxide were purchased from Aldrich. 4-Hydroxybenzene boronic acid, (4-bromo-phenyl)-acetonitrile, and tetrakis(triphenylphosphine)palladium(0) were purchased from Lancaster. H_2PtCl_6 was purchased from Showa Chemical. All materials were used as received. Trimethoxysilane was purchased from Fluka and used after distillation under vacuum.

4-Pent-4-enyloxy-benzaldehyde (1). In a round-bottom flask, a solution of 4-hydroxybenzaldehyde (0.31 g, 2.56 mmol), potassium carbonate (1.1 g, 7.6 mmol), and 18-crown-6-ether (0.13 g, 0.5 mmol) in 20 mL of tetrahydrofuran (THF) was stirred for 1 h at 75 °C. Then, 0.42 g of 5-bromo-1-pentene (2.8 mmol) was added dropwise, and the solution was stirred overnight at 75 °C. The reaction mixture was quenched with water, extracted with ethyl acetate, and dried over anhydrous magnesium sulfate. The ethyl acetate was evaporated under reduced pressure. Finally, the product was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane: 1/1) to give 0.43 g of product as an ivory-colored solid (yield = 89%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.88 (s, 1H); 7.87 (d, 2H); 6.99 (d, 2H); 5.84 (m, 1H); 5.03 (m, 2H); 4.05 (t, 2H); 2,24 (m, 2H); 1.92 (m, 2H). IR (KBr window, cm^{-1}): 1689 (CHO).

(4-Pent-4-enyloxy-phenyl)-acetonitrile (2). In a round-bottom flask, a solution of (4-hydroxy-phenyl)-acetonitrile (0.34 g, 2.56 mmol), potassium carbonate (1.1 g, 7.6 mmol), and 18-crown-6-ether (0.13 g, 0.5 mmol) in 20 mL of tetrahydrofuran (THF) was stirred for 1 h at 75 °C. Then, 0.42 g of 5-bromo-1-pentene (2.8 mmol) was added dropwise, and the solution was stirred overnight at 75 °C. The reaction mixture was quenched with water, extracted with ethyl acetate, and dried over anhydrous magnesium sulfate. After evaporation of the ethyl acetate under reduced pressure, the crude product was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane: 1/5) to give 0.5 g of product as an ivory-colored solid (yield = 97%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.22 (d, 2H); 6.88 (d, 2H); 5.84 (m, 1H); 5.03 (m, 2H); 3.96 (t, 2H); 3.68 (s, 2H); 2.22 (m, 2H); 1.88 (m, 2H). IR (KBr window, cm^{-1}): 2252 (CN).

2,3-Bis(4-pent-4-enyloxy-phenyl)-acrylonitrile (CNPPE). An equimolar mixture of **1** (0.28 g, 1.49 mmol) and **2** (0.35 g, 1.49 mmol) in *tert*-butyl alcohol (5 mL) was stirred at 50 °C for 1 h. Then, tetrabutylammonium hydroxide (TBAH) (1 M solution in methanol) (0.15 mL) was slowly added to the mixture dropwise and stirred for an additional 1 h. The product was collected by column chromatography (silica gel, ethyl acetate/*n*-hexane: 1/5) as a pale ivory-colored viscous liquid (yield = 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 (d, 2H); 7.56 (d, 2H); 7.34 (s, 1H); 6.94 (m, 4H); 5.84 (m, 2H); 5.04 (m, 4H); 4.02 (m, 4H); 2.25 (m, 4H); 1.93 (m, 4H).

2,3-Bis[4-(5-trimethoxysilyl)-pentyloxy-phenyl]-acrylonitrile (3). A mixture of **CNPPE** (0.44 g, 1.18 mmol) and H_2PtCl_6 (0.05 g, 0.12 mmol) in 50 mL of dry 1,2-dichloroethane was stirred for 30 min. Then trimethoxysilane (0.35 mL, 2.83 mmol) was added dropwise and the mixture was stirred for 48 h. Solvent and excess of trimethoxysilane were removed by evaporation-reduced pressure. The crude reaction mixture was purified by column chromatography (silica gel, chloroform) to give 0.57 g of product as a pale yellow solid (yield = 80%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.83 (d, 2H); 7.56 (d, 2H); 7.34 (s, 1H); 6.94 (m, 4H); 4.02 (m, 4H); 3.63 (s, 18H); 2.25 (m, 4H); 1.84 (m, 4H); 1.56 (m, 4H); 0.75 (m, 4H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 161.08; 160.06; 140.26; 131.27; 127.61; 127.42; 126.98; 119.14; 115.38; 115.31; 108.62; 68.46; 50.93; 29.81; 29.26; 22.88; 9.57. ^{29}Si NMR (200 MHz, $CDCl_3$): δ −41.41.

(4′-Hydroxy-biphenyl-4-yl)-acetonitrile (4). (4-Bromo-phenyl)-acetonitrile (1.4 g, 7.14 mmol), 4-hydroxybenzeneboronic acid (1 g, 7.25 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.08 g, 0.07 mmol) were dissolved in 60 mL of THF and 30 mL of 2 N sodium carbonate aqueous solution and reacted for 12 h at 77 °C. The reaction mixture was then poured into brine solution, extracted with ethyl acetate, and dried over anhydrous magnesium sulfate. Finally, the solvent was removed under reduced pressure. The crude reaction mixture was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane: 1/1) to give 1.1 g of product as a white solid (yield = 72%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.55 (d, 2H); 7.47 (d, 2H); 7.37 (d, 2H); 6.91 (d, 2H); 4.83 (s, 1H); 3.78 (s, 2H). IR (KBr window, cm^{-1}): 2167 (CN); 3363 (OH). MS (EI): Calcd for $C_{14}H_{11}NO$, 209.24; found, 209.

4′-Hydroxy-biphenyl-4-carbaldehyde (5). 4-Bromo-benzaldehyde (1.3 g, 7.03 mmol), 4-hydroxybenzeneboronic acid (1 g, 7.25 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.08 g, 0.07 mmol) were dissolved in 60 mL of THF and 30 mL of 2 N sodium carbonate aqueous solution and reacted for 12 h at 77 °C. The reaction mixture was then poured into brine solution, extracted with ethyl acetate, and dried with anhydrous magnesium sulfate. Finally, the solvent was removed under reduced pressure. The crude reaction mixture was purified by column chromatography (silica gel, tetrahhydrofurane/*n*-hexane: 1/2) to give 0.8 g of product as a white solid (yield = 56%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.04 (s, 1H); 7.93 (d, 2H); 7.71 (d, 2H); 7.55 (d, 2H); 6.94 (d, 2H); 4.98 (s, 1H). IR (KBr window, cm^{-1}): 1673 (CHO); 3417 (OH). MS (EI): Calcd for $C_{13}H_{10}O_2$, 198.22; found, 198.

2,3-Bis(4′-hydroxy-biphenyl-4-yl)-acrylonitrile (6). An equimolar mixture of **4** (0.4 g, 1.91 mmol) and **5** (0.38 g, 1.91 mmol) in

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methyl alcohol (4 mL) was stirred at 50 °C for 1 h. Tetrabutylammonium hydroxide (TBAH) (4.01 mL of a 1 M solution in methanol) was slowly added into the mixture dropwise and stirred for an additional 1 h. The reaction mixture was then neutralized by addition of 1 M HCl aqueous solution. The yellow precipitate was collected by filtration and washed with water (yield = 60%). ^{1}H NMR (300 MHz, DMSO): δ 9.68 (s, 2H); 8.08 (s, 1H); 8.02 (d, 2H); 7.77 (m, 6H); 7.63 (d, 2H); 7.58 (d, 2H); 6.88 (d, 4H). IR (KBr window, cm^{-1}): 2221 (CN); 3417 (OH). MS (FAB): Calcd for $C_{27}H_{19}NO_2$, 389.45; found, 389.

2,3-Bis(4′-pent-4-enyloxy-biphenyl-4-yl)-acrylonitrile (CNPBE). In a round-bottom flask, a solution of compound **6** (0.3 g, 0.63 mmol), potassium carbonate (0.33 g, 2.28 mmol), and 18-crown-6-ether (0.06 g, 0.25 mmol) in 40 mL of THF was stirred for 1 h at 75 °C. Then, 2.7 mL of 5-bromo-1-pentene was added dropwise, and the solution was stirred overnight at 75 °C. The reaction mixture was quenched with water, extracted with chloroform, and dried over anhydrous magnesium sulfate. The chloroform was then evaporated under reduced pressure. Finally, the crude product was purified by column chromatography (silica gel, dichloromethane) to give 0.35 g of product as a yellow solid (yield = 86%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.97 (d, 2H); 7.74 (d, 2H); 7.67 (d, 4H); 7.58 (m, 5H); 6.98 (d, 4H); 5.87 (m, 2H); 5.04 (m, 4H); 4.02 (m, 4H); 2.27 (m, 4H); 1.92 (m, 4H). IR (KBr window, cm^{-1}): 2221 (CN). MS (EI): Calcd for $C_{37}H_{35}NO_2$, 525.68; found, 525.

2,3-Bis[4′-(5-trimethoxysilyl)-pentyloxy-biphenyl-4-yl]-acrylonitrile (7). A mixture of **CNPBE** (0.44 g, 1.18 mmol) and H_2PtCl_6 (0.05 g, 0.12 mmol) in dry 1,2-dichloroethane was stirred for 30 min. Then, trimethoxysilane (0.35 mL, 2.83 mmol) was added dropwise and the mixture was stirred for 48 h. Solvent and excess of trimethoxysilane were evaporated under reduced pressure. Finally, the crude product was purified by column chromatography (silica gel, chloroform) to give 0.57 g of product as a pale yellow solid (yield = 80%). ^{1}H NMR (200 MHz, CDCl3): δ 8.00 (d, 2H); 7.78 (d, 2H); 7.72 (d, 4H); 7.57 (m, 5H); 7.03 (d, 4H); 4.02 (m, 4H); 3.63 (s, 18H); 2.25 (m, 4H); 1.84 (m, 4H); 1.56 (m, 4H); 0.75 (m, 4H). ^{13}C NMR (200 MHz, CDCl$_3$): δ 159.57; 141.50; 130.26; 129.73; 128.54; 128.41; 128.25; 126.72; 118.67; 115.44; 110.90; 68.42; 50.95; 29.88; 29.35; 22.90; 9.59. ^{29}Si NMR (200 MHz, CDCl$_3$): δ −41.41.

General Procedure for the Xerogel Synthesis. In a Schlenk flask, precursors and THF were mixed and stirred vigorously. The hydrochloric acid (37% in H_2O) was then added and the mixture was stirred for an additional 2 min. The stirring was then stopped to allow gelation in a steady state. The resulting gel was allowed to age for 8 days, after which it was crushed, washed with acetone and then ethanol, and finally dried for 24 h at 120 °C under vacuum.

Nanoparticle Preparation. Nanoparticles were prepared by a simple reprecipitation method.[20] Distilled water was slowly injected into the THF solution of the chromophore with vigorous stirring at room temperature, using a syringe pump. Before injection of the distilled water, both the distilled water and the chromophore solution were passed through a filter of 0.2 μm pore size. In all samples, the chromophore concentration (1×10^{-5} mol L^{-1}) was kept constant after distilled water injection.

Instrumentation. *X-ray Diffraction Spectroscopy.* The X-ray experiments were performed on an imaging plate 2D detector with a rotating copper anode apparatus (Cu Kα, $\lambda = 1.542$ Å) equipped with the focusing monochromator system OSMIC. Samples, which had been ground in an agate mortar under nitrogen, were placed in glass Lindemann capillary tube of diameter 1 mm and length 80 mm. An acquisition time of 2000−3000 s was used. The distance between source and detector was 180 mm, the plate diameter was 300 mm, and the beam size was 0.5 × 0.5 mm.

Polarizing Optical Microscopy (POM). Polarizing optical microscopy images of the material were obtained using a Laborlux12POLS polarizing microscope. Photographs were taken using a Leica Wild MPS28 camera.

^{29}Si NMR. ^{29}Si NMR spectra were recorded on an AM300 at 59.620 MHz, with 10 s acquisition time, 2 ms contact time, 7400 scans, and 5000 Hz rotation speed. Cross-polarization magic angle spinning (CP MAS) spectroscopy is not quantitative; however, it has been shown that single-pulse experiments did not reveal any significant variation in relative peak intensity from the CP MAS spectra in the case of these xerogels.[26,28,29] The spectral data cited are given with ±5% of reliability. Chemical shifts are indicated in ppm with respect to tetramethylsilane (TMS).

Porosimetry Measurements. Porosimetry measurements were performed either on a Micrometric Gemini III or on a Micrometritics ASAP 2010 porosimeter using N_2 at 77 K as the adsorbent. Samples were outgassed at 100 °C under a 0.1 mmHg vacuum before analysis. The equilibrium time was set to 5 s, and the specific area was calculated using the BET equation.

Thermogravimetric Analysis. Thermogravimetric analyses (TGA) were conducted using a NETZSCH STA409PC at a heating rate of 10 °C/min under a nitrogen atmosphere (50 mL min^{-1}).

Optical Properties Measurements. Absorption spectra were recorded using a Shimazu UV-1650PC spectrometer from 250 to 600 nm in 0.2 nm increments. Photoluminescence spectra were obtained using a Shimazu RF 5301 PC spectrophotometer.

Results and Discussion

Synthesis of Novel Fluorescent Precursors. Scheme 1 illustrates the chemical structure of the fluorescent anisotropic xerogels. The precursor containing the 1-cyano-1,2-bisbiphenyl-ethylene moiety (**7**) for the hybrid xerogel was conveniently synthesized according to Scheme 2. Two biphenyl compounds, **4** and **5**, were synthesized by the Suzuki coupling reaction of an aromatic boronic acid and aromatic bromide. Compounds **4** and **5** were then reacted via a tetrabutylammonium hydroxide (TBAH) catalyzed Knoevenagel condensation to give **6** (yield = 60%). Compound **6** was subsequently subjected to the Williamson reaction to give the vinyl-terminated intermediate, **CNPBE**. Finally, **CNPBE** was hydrosilylated with trimethoxysilane and platinum catalyst to give the target compound **7**. The yellow precursor powder was purified by column chromatography with chloroform eluent (yield = 80%). A simple phenylene cyanostilbene type precursor (**3**) was also synthesized as a reference sample showing much less intermo-

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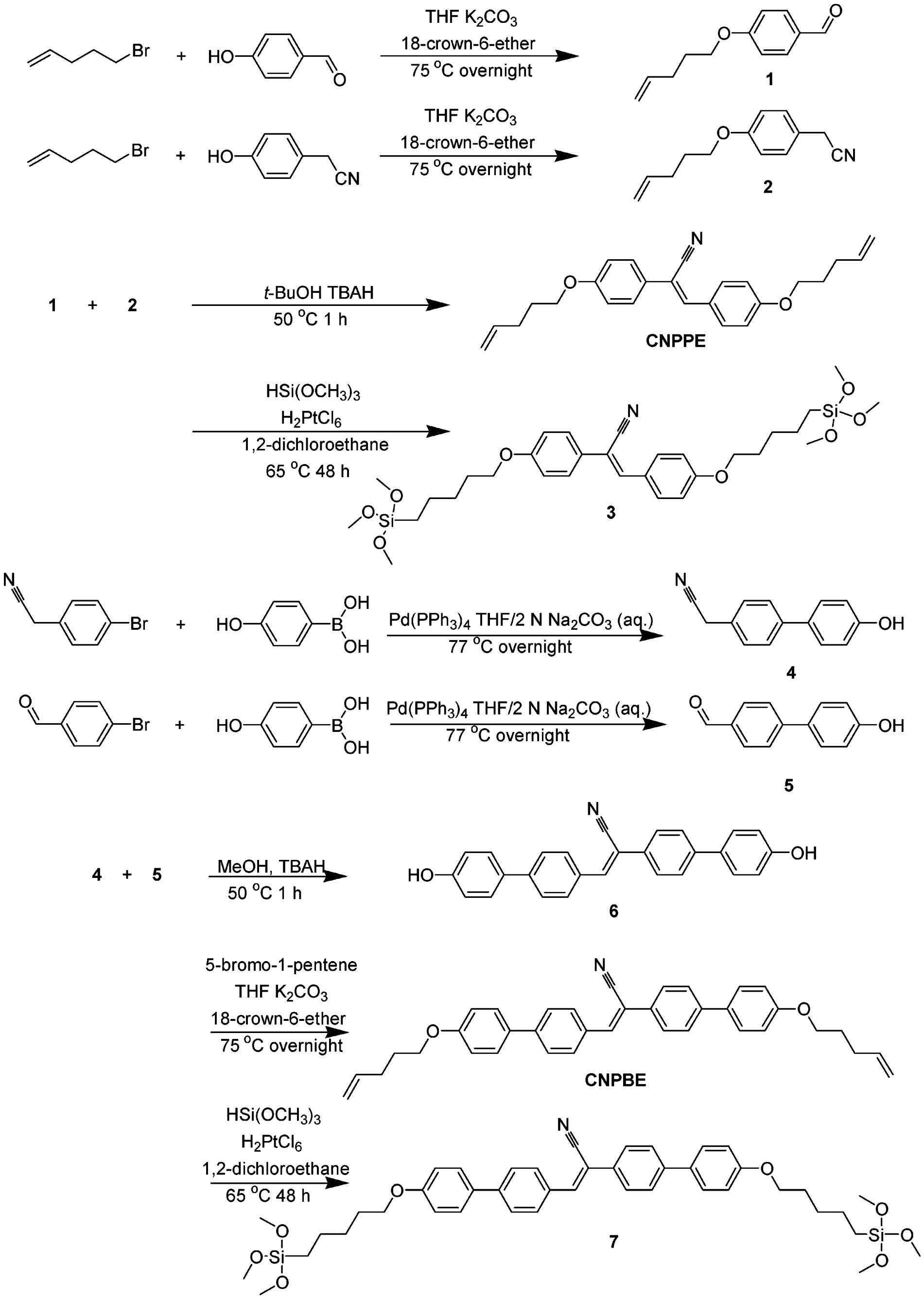
Scheme 2. Synthesis of CNPPE and CNPBE Bridged Precursors



lecular $\pi-\pi$ interactions. Compound **3** was synthesized from **1** and **2** via a procedure similar to that used to synthesize **7**. Although **CNPPE** has a structure similar to that of **CNPBE**, it was obtained as a viscous liquid due to its weaker intermolecular $\pi-\pi$ interactions and the solubilizing effect of the substituent alkyl chain.

Emission Properties of Fluorophoric Moiety. CNPBE showed a dramatic change in fluorescence intensity on going from the nonfluorescent isolated single molecules in THF solution to the strongly fluorescent nanoparticle suspension in THF/water mixture (Figure 1b). Isolated **CNPBE** was almost nonfluorescent ($\Phi_f = 0.005$), whereas the fluorescence quantum yield (Φ_f) of the nanoparticle suspension ($\Phi_f = 0.23$) was almost 50 times higher than that of the solution.[30] **CNPBE** molecules in dilute solution are elastically twisted[20] ("elasticity" means "reversible twisting" which is controlled by the intermolecular interactions), to show suppressed fluorescence emission.[20] In the condensed nanoaggregate state, by contrast, these units are forced to assume a planar conformation by favorable $\pi-\pi$ interaction forces, leading to AIEE.[20,21]

In recent years, enhanced emission in the solid state has been observed for a few organic molecules; this enhancement was interpreted in terms of the intra- and intermolecular

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(30) Fluorescence quantum yield (Φ_f) was calculated using 9,10-diphenylantracene (DPA) in benzene as a standard reference: Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic Press: New York, 1971.

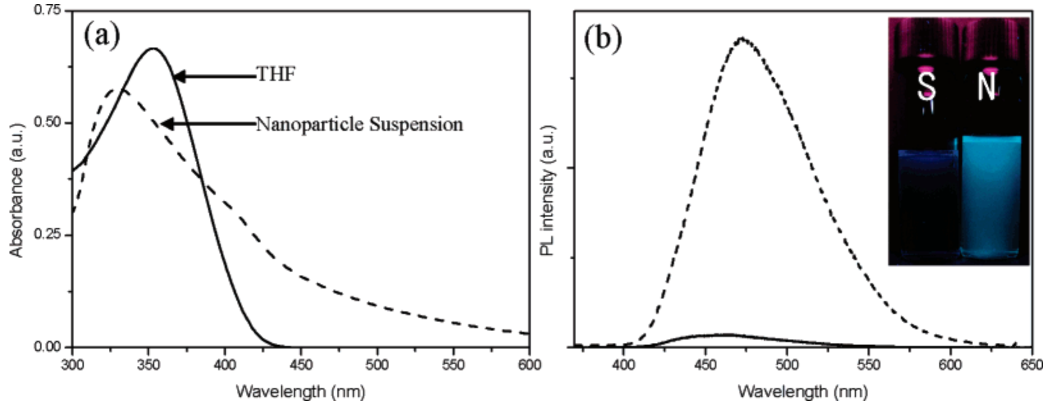

Figure 1. (a) UV−vis absorption spectra of **CNPBE** (1×10^{-5} mol L^{-1}) in THF (solid line) and its nanoparticle suspension in THF/water (1:4) mixture (dashed line). (b) Photoluminescence spectra of **CNPBE** (1×10^{-5} mol L^{-1}) in THF (solid line) and its nanoparticle suspension in a THF/water (1:4) mixture (dashed line). Inset photograph shows the fluorescence emission of **CNPBE** (1×10^{-5} mol L^{-1}) (S, solution; N, nanoparticle suspension) under 365 nm UV light illumination.

Table 1. Characteristics of the CNPPESi and CNPBESi Xerogels Prepared in THF as the Solvent with HCl as the Catalyst at 20 °C

	SSA[a] (m^2 g^{-1})	T_d[b] (°C)	chemical shift and polycondensation level (ppm (%))		
			T^2	T^3	level of condensation
CNPPESi	<10	317	−58.99 (56)	−64.77 (44)	81%
CNPBESi	<10	391	−58.01 (21)	−65.57 (79)	93%

[a] Specific surface area. [b] Thermal degradation temperature.

effects exerted by aggregation of fluorophores.[20,21,31,32] In these cases, the fluorescence enhancement is induced through intramolecular conformation changes and J-type aggregation, which suppress the nonradiative decay processes.[33] For most conventional fluorescent molecules, intermolecular face-to-face interaction is favored, which gives nonradiative deactivation (including H-aggregation), resulting in concentration quenching.[34] Very few systems have been found to exhibit fluorescence enhancement from H-type aggregation.[35] Even in systems where the fluorophoric moiety favors strong intermolecular interactions to form the parallel alignment in the aggregation state, bulky substituents in the fluorophoric units can induce slipover between the neighboring dye molecules, thereby reducing the probability of nonradiative deactivation.[35] **CNPBE** belongs to this class of materials. Compared to the absorption spectrum of **CNPBE** solution, the spectrum of the aggregated state exhibits a hypsochromic shift of the absorption maximum (Figure 1a), indicative of strong intermolecular $\pi-\pi$ interactions, resulting in the H-type aggregation of the fluorophores. At the same time, aggregation-induced planarization combined with steric effects of the bulky and polar cyano functionality substituted on the vinyl group leads to strong fluorescence emission in the aggregated state. Collectively, the present results show that the **CNPBE** unit has a strong self-assembling power accompanied by the enhanced fluorescence emission.

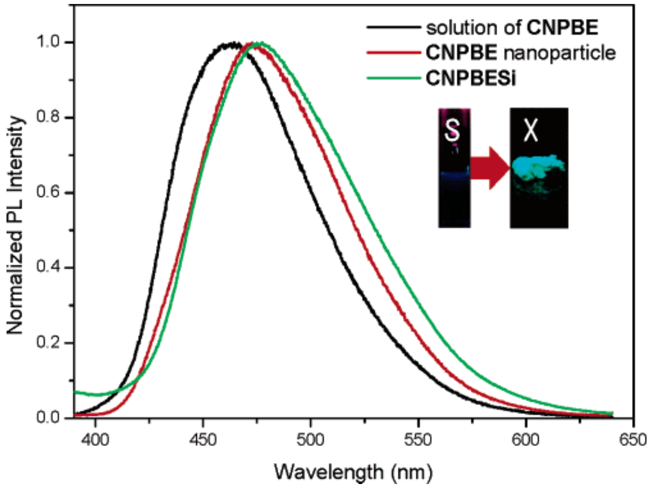

Figure 2. Emission spectra of **CNPBE** and **CNPBESi**. (inset: fluorescence image of **CNPBESi** (X) and solution of **CNPBE** (S) under UV irradiation at 365 nm).

Preparation and Structural Analysis of Xerogels. Hydrolysis and polycondensation of precursors **3** and **7** were carried out by a classical sol−gel procedure under highly acidic conditions to yield **CNPPESi** and **CNPBESi** (see Scheme 1 for their structures). Initially, a clear and homogeneous precursor solution was obtained by mixing either **3** or **7** at 20 °C in the following molar ratio of precursor/water/THF/HCl solution: 1/3/20/0.5 for **CNPPESi** and 1/3/100/0.5 for **CNPBESi**. The sol−gel reaction of the precursor solutions proceeded at 20 °C. The solution of compound **3** formed a gel within a few minutes to give **CNPPESi**, whereas the solution of **7** almost immediately yielded **CNPBESi** as an aggregate of small particles. The rapid gelation of **7** is ascribed to the strong intermolecular $\pi-\pi$ stacking forces between the precursor units. After aging for 8 days, followed by drying in a vacuum oven at 120 °C, the final xerogels were collected and analyzed. Porosimetry

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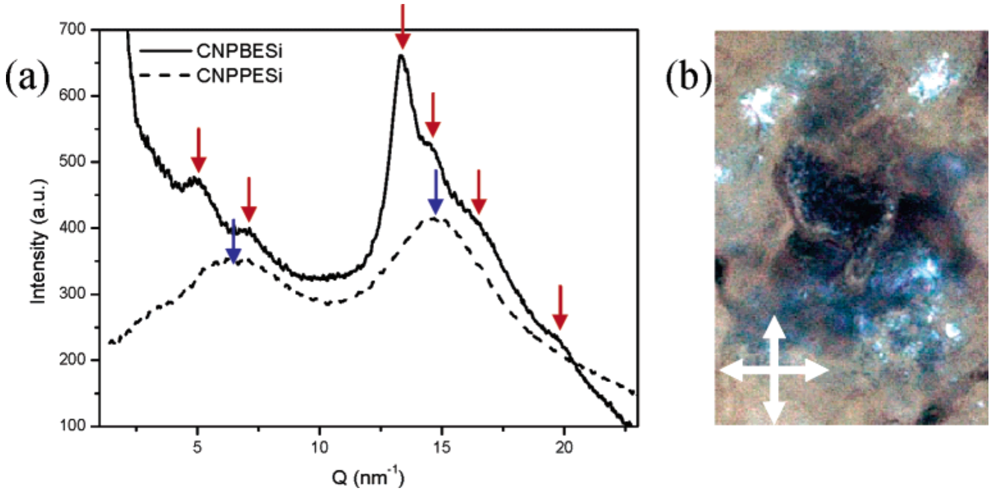

Figure 3. (a) X-ray powder diffraction patterns of **CNPBESi** and **CNPPESi** and (b) **CNPBESi** observed by polarizing optical microscopy.

Table 2. X-ray Diffraction Characteristics of CNPPESi and CNPBESi

	Q (nm^{-1})	*d* (nm)
CNPPESi	6.5; 14.5	0.43; 0.96
CNPBESi	5.0; 7.1; 13.3; 14.5; 16.5; 20.0	0.31; 0.38; 0.43; 0.47; 0.88; 1.25

measurements of **CNPPESi** and **CNPBESi** powders with nitrogen as the absorbent revealed that both xerogels were nonporous solids (Table 1), consistent with previous reports that xerogels formed from precursors with flexible chains using HCl as a catalyst are nonporous solids.[24,25] Formation of such a dense medium is a direct consequence of the strong intermolecular interactions between the organic bridges. As summarized in Table 1, both xerogels were highly cross-linked solids as deduced from ^{29}Si NMR CP MAS analyses[26,28,29] with high thermal stability (above 300 °C).

Characterization of the Xerogels. To examine the optical properties of the xerogels, a small amount of the precursor solution was placed in a thin sandwich-type quartz cell and the gelation was effected in situ.[11] Much the same as **CNPBE**, precursor compound **7** showed very low fluorescence quantum yield ($\Phi_f = 0.01$), while the gelation product **CNPBESi** exhibited strong and bathochromically shifted emission that coincided exactly with the emission spectrum of the H-type aggregate of the fluorophoric moiety, clearly reflecting the parallel alignment of the organic bridge in xerogel structure (Figure 2). This strong fluorescence emission behavior of **CNPBESi** is thus unambiguously attributed to the ordered structure in the xerogel state driven by the strong intermolecular $\pi-\pi$ interaction between the organic bridges to form parallel alignment.

Although the chemical structures of precursors **3** and **7** differ only in the number of aromatic units, molecular stacking and relevant morphologies in the xerogels of **CNPPESi** and **CNPBESi** are very different, as evidenced by X-ray diffraction analysis (Figure 3a and Table 2). In the case of **CNPPESi**, X-ray powder diffraction showed broad signals in the 2θ range of 1.4° to 12.6°, indicating that the xerogel has only very short-range order. This observation suggests that the intermolecular $\pi-\pi$ interactions are insufficient to provide regular and periodic packing. A similar situation has been observed for materials prepared from similar monophenyl-containing precursors[23,24,27] and for simple polysilsesquioxanes.[10,11] In contrast, **CNPBESi** exhibited a set of six signals in the X-ray diffraction spectrum that clearly indicate the presence of long-range-order packing, in terms of periodical orientation and positioning within the xerogel structure. When the xerogels were observed by polarizing optical microscopy, the **CNPPESi** was nonbirefringent and thus no image was to be seen under POM. In contrast, **CNPBESi** exhibited birefringence throughout the xerogel (Figure 3b). This birefringence reveals the anisotropy of the material and, together with the X-ray powder diffraction and fluorescence emission spectral data, indicates that the self-organization of the biphenyl cyanostilbene bridges through intermolecular $\pi-\pi$ interactions is very efficient in this material.

In conclusion, we synthesized a novel anisotropic and fluorescent xerogel of bridged silsesquioxanes (**CNPBESi**) with an organic bridge with strong intermolecular $\pi-\pi$ interactions. Bright bluish green fluorescence emission from **CNPBESi** was attributed to the aggregation-induced enhanced emission (AIEE) of the organic bridge structure.

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