

Blue electroluminescence from polyhedral oligomeric silsesquioxane containing spirobifluorene trimers



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ABSTRACT

We synthesized and characterized a new polyhedral oligomeric silsesquioxane (POSS)-based deep blue light-emitting nanoparticle. A spirobifluorene trimer (SFL3) was used as the blue fluorescent chromophore. The allyl-functionalized SFL3 was introduced to octakis(dimethylsiloxy)silsesquioxane via hydrosilylation to afford POSS-SFL3. POSS-SFL3 was completely soluble in common organic solvents such as chloroform, tetrahydrofuran, and p-xylene, and formed a uniform thin film upon spin-coating. The UV-vis absorption and photoluminescence (PL) emission maxima of POSS-SFL3 were 356 and 425 nm, respectively. An electroluminescent (EL) device with configuration ITO/PEDOT:PSS(40 nm)/poly-TPD(50 nm)/POSS-SFL3 (30 nm)/TPBI (40 nm)/LiF (0.5 nm)/Al (100 nm) was fabricated and showed a stable deep-blue electroluminescence with an electroluminescence (EL) maximum at 431 nm and CIE chromaticity coordinates of (0.17, 0.10).

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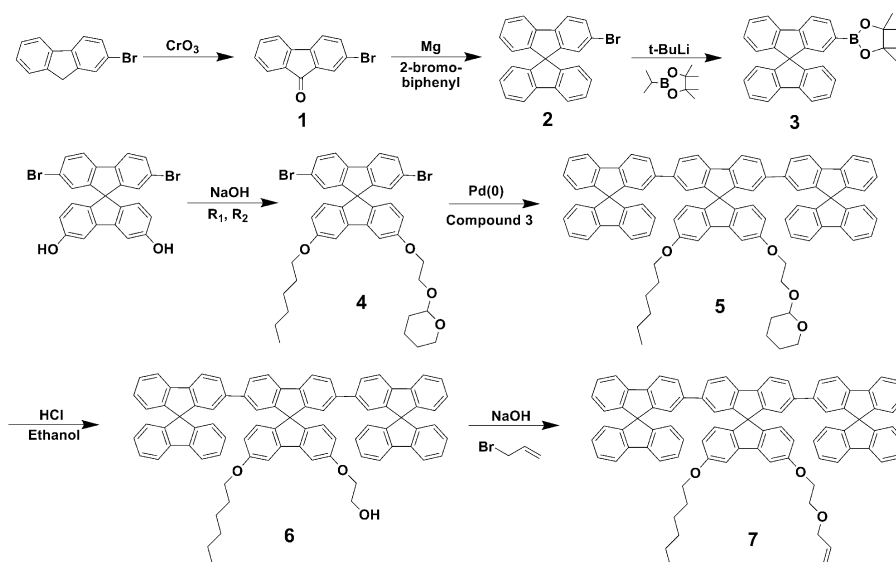
1. Introduction

Organic light-emitting diodes (OLEDs) have attracted much scientific and technological interest since the first report of a high-efficiency OLED by Tang and Van Slyke [1]. Over the past two decades, an enormous number of light-emitting organic molecules have been developed for OLEDs [2–4]; as a result, full-color OLEDs have been successfully commercialized for small mobile electronic devices and also recently for large television sets by overcoming the classic issues of low device efficiency, poor color purity, and short lifetime. In contrast, the speed of the development of technology for polymer light-emitting displays (PLEDs) is much slower even though PLEDs have many advantages over OLEDs, such as the cost-effective solution-based manufacturing process [5–8]. The slow development is caused by the drawbacks of polymeric materials as emissive materials for electronic displays, such as molecular-weight distribution, various types of defects, labile end groups on polymer chains even after end-capping, and difficulties in removing impurities, which result in PLEDs with low efficiency, poor reliability, and short lifetimes.

To solve these problems, we focused on organic/inorganic hybrid materials such as polyhedral oligomeric silsesquioxane (POSS) derivatives as emissive materials for solution-based light-emitting displays because they are well-defined single molecules that do not contain end groups or defects and have good thermal and mechanical stability. Polyhedral oligomeric silsesquioxanes have a unique cage-like structure with nanoscale dimensions [9–16]; eight organic functional groups can be introduced to each POSS unit, which enables interesting chemistry and molecular engineering [17]. The molecular weights of POSS derivatives can reach around 10,000 with medium-sized light-emitting chromophores, which would impart sufficient mechanical strength [18–20]. Originally, we reported the synthesis and electroluminescent (EL) properties of POSS-based EL materials [21–24]. The terfluorene-containing POSS derivative (POSS-FL3) showed good film-forming properties and deep-blue photoluminescence (PL) in solution and as a solid film. However, a very high additional long wavelength emission was observed in its EL, which could be due to the formation of keto defects or excimers [21]. Blue electroluminescence could not be obtained, even when deep-blue light-emitting phenylanthracene chromophores were attached because of the formation of excimers via strong inter-chromophore interaction [25]. Blue PL from POSS-based light-emitting materials has been reported by other groups; however, blue EL has not yet been reported [26,27].

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Scheme 1. Synthetic routes toward SFL3.

In this paper, we report the synthesis and luminescent properties of a POSS-based blue EL nanoparticle, POSS-SFL3. To suppress the excimer emission by minimizing the inter-chromophore interaction in the solid state, we introduced a spirobifluorene trimer (SFL3) to POSS as a blue light-emitting chromophore. The SFL3 unit is known to effectively suppress the formation of excimers in light-emitting molecules and polymers. The synthetic routes for SFL3 and POSS-SFL3 are shown in Schemes 1 and 2, respectively.

2. Experimental

2.1. Materials

2-Bromofluorene, 1,2-dichloroethane, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 2-(2-bromoethoxy)tetrahydro-2H-pyran, tetrakis(triphenylphosphine)palladium, *tert*-butyllithium, 1,3,5,7,9,11,13,15-octakis-(dimethylsilyloxy)-pentacyclo-[9.5.1.1.^{3,9}1.^{5,15}1^{7,13}]-octasiloxane, tetrabutylammoniumbromide (TBAB), allyl bromide, platinum-(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex [Pt(dvs)], Aliquat-336[®], and chloroform were purchased from Aldrich Chemical Co., Inc. and used without further purification. Cerite-545, 35% aqueous hydrochloric acid, chloroform, ethyl acetate, tetrahydrofuran (THF), toluene, anhydrous magnesium sulfate (MgSO₄), potassium carbonate (K₂CO₃), and sodium hydroxide (NaOH) were purchased from Junsei Chemical Co. 2-Bromobiphenyl and bromohexane were purchased from TCI Chemical Co. 2,7-Dibromo-11,14-dihydroxyspirobifluorene was synthesized according to reported procedures [28,29]. Poly(ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) (Bayer), which was used in the LED fabrication, was filtered through a 0.45 μm nylon filter prior to spin coating. THF was freshly distilled and all other organic solvents were used without further purification.

2.2. Measurements and LED fabrication

¹H and ¹³C NMR spectra were recorded using a Bruker AM-400 spectrometer. Mass spectra were recorded using a Waters ZQ2000 LC/MS spectrometer and elemental analysis was performed using an EA 1110 Fisons analyzer. UV-vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer, and the baseline corrections and normalizations were carried out using Microsoft Excel software. The thermal stability and thermal transition temperature

were observed using a Q-50 (TA Instruments) thermogravimetric analyzer and 200F3 (NETZSCH) differential scanning calorimeter (DSC), respectively, under a nitrogen atmosphere at a heating rate of 10 °C/min. Photoluminescent emission spectra were recorded using dilute (10⁻⁶ M) solutions on a Shimadzu RF 5301 PC fluorometer. Cyclic voltammetry (CV) was performed on AUTO-LAB/PGSTAT12 at room temperature using a three-electrode cell in a solution of tetrabutylammonium tetrafluoroborate (TBABF₄; 0.10 M) in acetonitrile at a scan rate of 50 mV/s. A film of POSS-SFL3 was prepared by dipping platinum working electrodes into the solution followed by air-drying. A platinum wire and Ag/Ag⁺ electrode were used as the counter and reference electrodes, respectively. The EL devices were fabricated as follows: First, a glass substrate was coated with a transparent layer of indium tin oxide (ITO) and then thoroughly cleaned by successive sonication treatments in acetone, isopropyl alcohol, and distilled water. The resulting glass/ITO system was dried under nitrogen gas and then by heating at 100 °C. A film of poly-TPD was prepared by spin coating a chloroform solution, and POSS-SFL3 films were prepared from different concentrations of solutions in *p*-xylene containing 1.0–3.0 wt%, respectively. Uniform films with thicknesses of around 20–30 nm were easily obtained for POSS-SFL3s, respectively.

2.3. Synthesis of POSS-SFL3

2.3.1. Synthesis of 2-bromo-fluorene-9-one (1)

Acetic anhydride (300 mL) was added to a solution of 2-bromofluorene (10 g, 0.04 mol) in a 1000 mL round-bottom flask and stirred for 10 min. Chromium oxide (CrO₃; 7.8 g, 0.078 mol) was slowly added to the flask at room temperature for 2 h. After the reaction completed, distilled water was added to the flask and the mixture was filtered; this procedure was repeated three times. Finally, the product was washed with 2-propanol. The product was dried *in vacuo*, affording 9.8 g of the desired product as a yellow solid. Yield: 9.8 g (95%). ¹H NMR (CDCl₃, ppm): δ 7.68 (s, 1H), 7.6–7.5 (m, 2H), 7.45–7.4 (d, 2H), 7.35–7.25 (m, 2H). ¹³C NMR (CDCl₃, ppm): δ 187.0, 138.9, 138.2, 137.2, 136.7, 136.0, 133.9, 132.7, 130.6, 129.3, 127.1, 121.7. Anal. Calcd for C₁₃H₇BrO: C, 60.26; H, 2.72. Found: C, 60.58; H, 2.96.

2.3.2. Synthesis of 2-bromo-spiro-bifluorene (2)

Magnesium (1.19 g, 0.05 mol) was inserted into a two-neck 50 mL round-bottom flask and dried *in vacuo*; a small amount of THF was added to the flask under a nitrogen atmosphere.

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