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Synthesis of Multi-Functional POSS Emitters for OLED Applications

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Three separate organic, fluorescent emitter molecules with emission spectra corresponding to either blue, orange, or yellow have been covalently attached to an inorganic polyhedral oligomeric silsesquioxane (POSS) core in several controllable combinations. We were able to functionalize POSS with eight of the same emitters or a combination of two different emitters (i.e., blue and orange or blue and yellow). After purification, monodisperse products of the desired ratio of emitters attached to POSS were obtained. Solution and thin-film photoluminescence spectra were measured and compared for both the free emitters and the functionalized POSS. All POSS emitter materials have shown an increase in thermal stability over their free emitter counterparts and were able to be spincoated from solution for the fabrication of OLED devices.

Introduction

Organic electroluminescent devices capable of emitting white light are desirable due to their potential utility in displays and in solid-state lighting applications. White organic light-emitting diodes (WOLED)s with high color purity and brightness exceeding 2000 cd/m^2 have been demonstrated at least since 1994.[1,2] Several strategies have been employed to generate white light by electroluminescence (EL) including devices utilizing multiple-emitting layers (red, green, and blue) fabricated by vacuum deposition of small molecules,[2] a single-emitting layer doped with multiple emitters of different colors,[1,3] blends of different color-emitting polymers,[4,5] excimers[6,7] or "electromers",[8] and emission from a semiconducting polymer. Efficient and bright, small molecule-based WOLEDs tend to require relatively complex multi-layer structures reaching eight organic layers in some cases.[9] In most published results, the spectrum of the emitted light is voltage dependent, and the device is eventually amenable to differential aging and potential aggregation of the dopants that results in a significant shift in color emission and reduced device stability. On the other hand, the simpler white-emitting polymer-based structure[10] is lagging in performance behind the small molecule. Although attractive due to lower cost processing, polymers currently cannot be purified to levels similar to those of small molecules. It is therefore important to seek an alternate material system that encompasses the benefits of small molecules (e.g., high levels of purity) and polymers (e.g., low processing cost and simple device architecture). One approach to accomplish this is to incorporate small molecules in a polymeric host; however, aggregation of such molecules will eventually degrade the WOLED performance.

Dendrimers or dendronized polymers have been used in OLED studies[11−15] and have yielded efficient OLEDs using simple processing techniques similar to what is used in polymer-based OLEDs. It has been demonstrated that adding dendritic bulky moieties can effectively suppress the formation of aggregation[11−13] and reduce self-quenching of luminescence due to intermolecular interactions.[14] However, and

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to the best of our knowledge, published reports in this area focus exclusively on single color emission (e.g., green).[15] Also, the tedious synthetic procedures of producing most dendrimers make them unpractical. An efficient alternative to a typical organic dendritic core is the use of a new class of inorganic cores known as polyhedral oligomeric silsesquioxanes (POSS).[16] The cubic form of POSS has the chemical formula $R_8Si_8O_{12}$ and consists of a rigid silica-like inorganic core that can be covalently linked to eight organic R groups. These molecules are excellent platforms for nanotechnology applications due to their perfectly defined spatial geometry that can be made to have a great variety of properties (e.g., charge transport, light absorption and emission, etc.).

Recently, POSS has been examined for its use in new hybrid materials for applications in EL devices. It is reported that semiconducting polymers containing POSS segments, when used in EL devices, exhibit better thermal stability, higher brightness, and higher external quantum efficiency as compared to the corresponding parent polymers.[17] Sellinger et al.[18] reported the synthesis of an octavinyl POSS substituted with a hole-transport moiety via Heck coupling and most recently reported the synthesis of pyrene substituted POSS as light-emitting materials in OLEDs.[19] Xiao et al.[20] reported the synthesis of an oligophenylene functionalized POSS utilizing a Grignard mechanism. The POSS substituted products in both of the previously mentioned systems proved to have superior thermal properties and device performance than the substituent that was not incorporated onto the POSS core. However, both of these methods sometimes yielded mixtures of multi-substituted POSS compounds, and due to the nature of the reactions, monodisperse POSS materials were difficult to isolate. Imae and Kawakami[21] reported the synthesis of a perfectly octa functionalized carbazole substituted POSS via a hydrosilylation reaction of 9-vinylcarbizole with octakis(dimethylsilyloxy)-POSS. The small size of the vinylcarbazole group may have facilitated the complete substitution on POSS.

In this paper, we report the synthesis of macromolecular materials comprised of an inorganic octakis(dimethylsilyloxy)-POSS core (**1**) and organic fluorescent emitters covalently attached either monochromatically or in a combination of mixed emitters. To the best of our knowledge, it is the first report of two different fluorescent emitters being attached to one POSS core in a controlled ratio. The primary emitters chosen for this work include a fluorene-based blue emitter (**2**, 450 nm), a donor−accepter fluorescent orange emitter (**3**, 610 nm), and its analogue yellow emitter (**4**, 574 nm).

As shown in Chart 1, two categories of POSS emitter materials were synthesized: (1) monochromatically functionalized blue, orange, and yellow POSS materials (**POSS(B)$_8$**, **POSS(O)$_8$**, and **POSS(Y)$_8$** (where **B**, **O**, or **Y** refer to blue-emitting, orange-emitting, or yellow-emitting, respectively) and (2) POSS containing a combination of blue and orange emitters in three different ratios, **POSS(B)$_7$(O)$_1$**, **POSS(B)$_6$(O)$_2$**, and **POSS(B)$_5$(O)$_3$**. **POSS(B)$_7$(Y)$_1$**, the analogue of **POSS(B)$_7$(O)$_1$** using the yellow emitter (**4**) in place of the orange emitter, was also synthesized for comparison of the PL and EL characteristics. All materials were characterized by NMR, MALDI-TOF, DSC, TGA, UV−vis, and photoluminescence spectra.

Experimental Procedures

General Information. All nonaqueous reactions were carried out under a dry argon atmosphere unless stated otherwise. Octakis(dimethylsilyloxy)-POSS (**1**) was received from Aldrich. All other reagents and solvents were received from Aldrich or Gelest and were used as received unless indicated otherwise. THF was freshly distilled from Na/benzophenone before use. Column chromatography was performed using silica gel from ICN SiliTech (32−63 μm). The NMR spectra data were collected using a JEOL ECL-400. Fluorescence measurements were performed on a Jobin Yvon Fluromax 3 luminescence spectrometer. UV−vis spectra were recorded on a Varian Cary 50 Scan spectrophotometer. DSC measurements were performed on a Seiko Exstar 6000 DSC 6200. TGA was performed on a PerkinElmer Pyris.

Blue Emitter (2). 2,7-Dibromofluorene was treated with LDA in THF at room temperature, and then methyl iodide was added at −78 °C to make 9-methyl-2,7-dibromofluorene, which was further treated with KOH at room temperature and then reacted with 6-chloro-1-hexene to obtain 9-methyl-9-(1′-hexene)-2,7-dibromofluorene. The di-bromide groups of 9-methyl-9-(1′-hexene)-2,7-dibromofluorene were first converted to di-aldehyde groups by treatment of *t*-BuLi and DMF at −78 °C in THF, then coupled with diphenylmethane-diethoxy phosphate in the presence of potassium *t*-butoxide to make the final blue emitter **2** at an overall yield of 39%.[22]

Orange Emitter (3). 4-Bromo-*N*,*N*-diphenyl aniline was treated with *t*-BuLi at −78 °C in THF and reacted with 6-chloro-1-hexene to make 4-(1′-hexene)-*N*,*N*-diphenyl aniline. The aldehyde group was installed on the para-position of one of the two phenyl groups by treatment of 4-(1′-hexene)-*N*,*N*-diphenyl aniline with $POCl_3$ in DMF at 90 °C. The final orange emitter **3** was then synthesized by Knovenagel condensation with 4-(dicyanomethylene)-2-(*t*-butyl)-4*H*-pyran[23] in the presence of piperidine-DMAP under reflux in acetonitrile with an overall yield of 15%.[22]

Yellow Emitter (4). The synthesis of the yellow emitter began with reacting diphenylamine with allyl bromide and NaOH in DMSO at 90 °C. The product, allyldiphenylamine, was purified by column chromatography (100% hexanes). The rest of the synthesis was similar to the procedure followed for the orange emitter (**3**).[22] The final product (**4**) was isolated as dark red sheets at an overall yield of 35%.

Typical Monochromatic POSS(R)$_8$ Synthesis. The monochromatically functionalized POSS materials were prepared via hydrosilylation of octakis(dimethylsilyloxy)-POSS (**1**) with an

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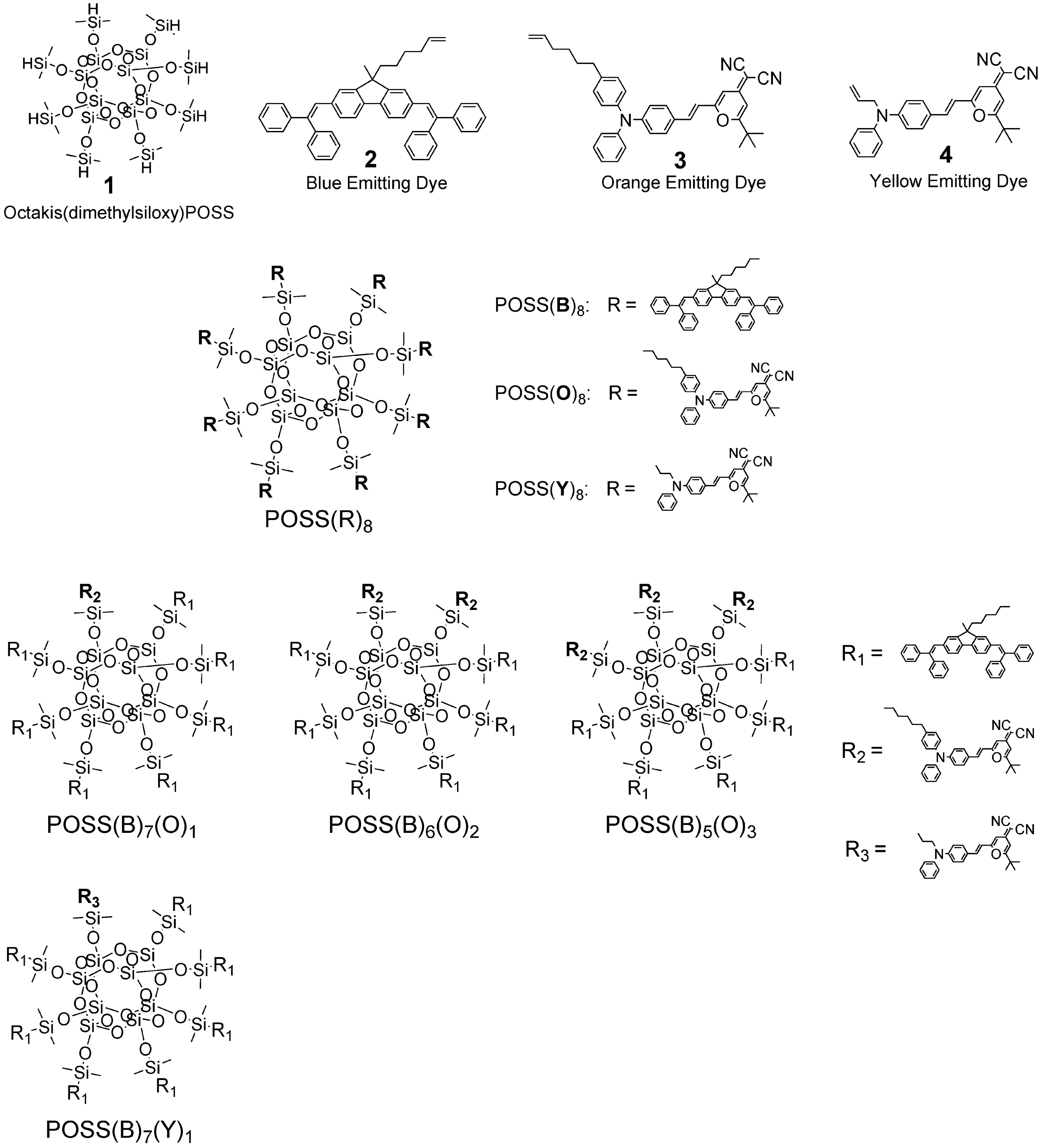
Chart 1. Structures of Materials Used in This Study



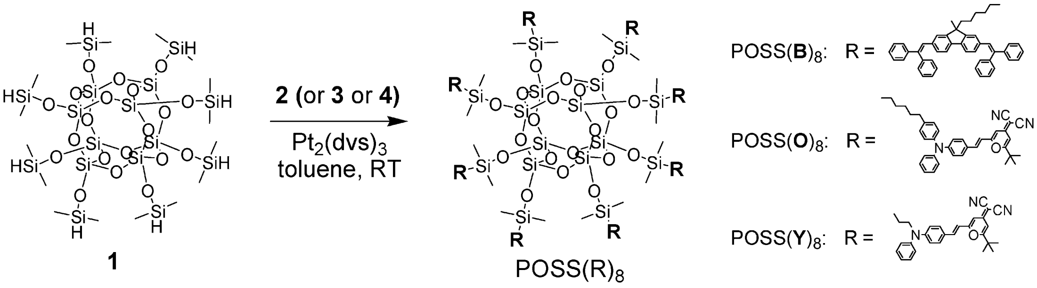
excess of the organic emitter containing a terminal alkene in the presence of $Pt_2(dvs)_3$ with anhydrous toluene as the solvent. The pure octa functionalized materials were obtained after column chromatography.

POSS(B)8. A round-bottomed flask was charged with a stir bar, 1,3,5,7,9,11,13,15-octakis(dimethylsilyloxy)pentacyclo-[9.5.1.1.^{3,9}1.^{5,15}1^{7,13}]-octasiloxane(octakis(dimethylsilyloxy)-POSS, **1**) (340 mg, 0.334 mmol), **2** (1.65 g, 2.67 mmol), and dry toluene (5 mL). $Pt_2(dvs)_3$ (the platinum-divinyl tetramethyldisiloxane complex) (0.05 mL, 2% Pt wt solution in xylene) was added, and the reaction mixture was stirred at room temperature under positive argon pressure for 2 h. The toluene was evaporated in vacuo, and **POSS(B)$_8$** was isolated chromatographically using 3:2 dichloromethane/hexanes to yield 1.16 g (60%) as yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.33 (d, 16H), 7.29−7.14 (m, 160H), 7.01−6.96 (m, 32H), 6.73 (s, 16H), 1.38−1.34 (m, 16H), 1.10−1.08 (m, 16H), 0.97−0.86 (m, 56H), 0.44−0.34 (m, 32), 0.00 (s, 48H). MS (MALDI-TOF): Calcd for $C_{400}H_{392}O_{20}Si_{16}$, 5968.8; found, 5968.5

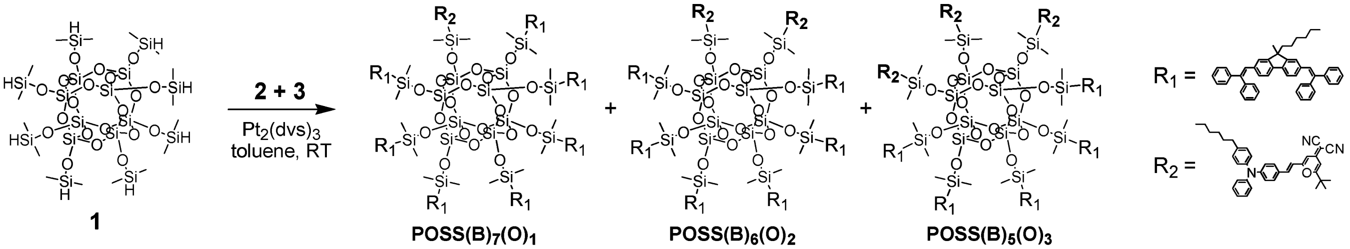
POSS(O)$_8$. Similar procedure as **POSS(B)$_8$**. Yield: 61%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.23 (m, 40H), 7.09−6.94 (m, 72H), 6.60−6.48 (m, 24H), 2.56−2.53 (t, 16H), 1.59−1.56 (m, 16H), 1.39−1.31 (m, 120H), 0.61 (m, 16H), 0.13 (s, 48H). MS (MALDI): MS (MALDI-TOF): Calcd for $C_{320}H_{352}N_{24}O_{28}Si_{16}$, 5431.7; found, 5432.0.

POSS(Y)$_8$. Similar procedure as **POSS(B)$_8$**. Yield: 47%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.09 (m, 64H), 6.67−6.65 (m, 16H), 6.54−6.39 (m, 24H), 3.59 (m, 16H), 1.58 (m, 16H), 1.34 (s, 72H), 0.56−0.52 (m, 16H), 0.05 (s, 48H). MS (MALDI-TOF): Calcd for $C_{248}H_{272}N_{24}O_{28}Si_{16}$, 4486.3; found, 4487.6

Scheme 1. Synthetic Scheme of Monochromatic POSS



Scheme 2



Mixed Functionalized POSS Materials. The synthesis of mixed functionalized POSS materials (**POSS(B)$_7$(O)$_1$**, **POSS(B)$_6$(O)$_2$**, and **POSS(B)$_5$(O)$_3$**) is represented by the following procedure: a round-bottomed flask was charged with a stir bar, octakis(dimethylsilyloxy)-POSS (**1**, 340 mg, 0.334 mmol), **3** (277 mg, 0.501 mmol), and anhydrous toluene (5 mL). Pt$_2$(dvs)$_3$ (0.05 mL, 2% Pt wt solution in xylene) was introduced into the solution, and the reaction mixture was stirred at room temperature under positive argon pressure for 30 min. A solution of **2** (1.65 g, 2.67 mmol) in anhydrous toluene (15 mL) was added, and the reaction mixture was allowed to stir at room temperature for 2 h. The toluene was evaporated in vacuo, and **POSS(B)$_7$(O)$_1$** was separated chromatographically using 3:2 dichloromethane/hexanes ($R_f = 0.24$) to yield 513 mg (26%). **POSS(B)$_6$(O)$_2$** and **POSS(B)$_5$(O)$_3$** were then separated using 100% dichloromethane (R_f = 0.60 and 0.29, respectively) to yield 348 mg (18%) and 179 mg (9%) respectively.

POSS(B)$_7$(O)$_1$. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.37−6.94 (m, 196H), 6.74 (s, 14H), 6.61−6.47 (m, 3H), 2.50−2.46 (t, 2H), 1.51 (m, 2H), 1.39−1.36 (m, 23H), 1.26 (m, 6H), 1.13 (m, 14H), 0.93 (m, 49H), 0.51−0.36 (m, 30H), 0.02 (m, 48H). MS (MALDI-TOF): Calcd for $C_{390}H_{387}N_3O_{21}Si_{16}$, 5901.6; found, 5901.2. Anal. Calcd for $C_{390}H_{387}N_3O_{21}Si_{16}$: C, 79.37; H, 6.61; N, 0.71. Found: C, 78.51; H, 7.10; N, 0.97.

POSS(B)$_6$(O)$_2$. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.37−6.94 (m, 184H), 6.74 (s, 12H), 6.61−6.47 (m, 6H), 2.50−2.46 (m, 4H), 1.51 (m, 4H), 1.39−1.36 (m, 30H), 1.27 (m, 12H), 1.15 (m, 12H), 1.00−0.94 (m, 42H), 0.50−0.36 (m, 28H), 0.03 (m, 48H). MS (MALDI-TOF): Calcd for $C_{380}H_{382}N_6O_{22}Si_{16}$, 5834.5; found, 5834.5. Anal. Calcd for $C_{380}H_{382}N_6O_{22}Si_{16}$: C, 78.23; H, 6.60; N, 1.44. Found: C, 77.52; H, 6.89; N, 1.83.

POSS(B)$_5$(O)$_3$. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.37−6.94 (m, 172H), 6.74 (s, 10H), 6.60−6.47 (m, 9H), 2.51−2.49 (t, 6H), 1.51 (m, 6H), 1.39−1.36 (m, 37H), 1.26 (m, 18H), 1.13 (m, 10H), 1.00−0.93 (m, 35H), 0.53−0.37 (m, 26H), 0.04 (m, 48H). MS (MALDI-TOF): Calcd for $C_{370}H_{377}N_9O_{23}Si_{16}$, 5767.4; found, 5767.6. Anal. Calcd for $C_{370}H_{377}N_9O_{23}Si_{16}$: C, 77.05; H, 6.59; N, 2.19. Found: C, 76.03; H, 6.75; N, 2.41.

POSS(B)$_7$(Y)$_1$. Similar procedure as **POSS(B)$_7$(O)$_1$**. Yield: 20%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.37−7.15 (m, 164H), 7.01−6.97 (m, 28H), 6.73 (s, 14H), 6.63−6.61 (m, 1H), 6.53−6.49 (m, 2H), 3.55 (t, 2H), 1.55 (m, 2H), 1.38−1.32 (m, 14H), 1.31 (s, 9H), 1.11 (m, 14H), 0.92 (m, 49H), 0.45−0.32 (m, 30H), 0.01 (s, 48H). MS (MALDI-TOF): Calcd for $C_{381}H_{377}N_3O_{21}Si_{16}$, 5783.5; found, 5782.8

EL Device Experimental Procedures. Polymer poly(*N*-vinylcarbazole) (PVK) and the electron-transporting additive 2-(4-biphenylyl)-5-(4-*t*-butylphenyl)1,3,4-oxadiazole (PBD) were used as a two part host. Equal weights of PVK to PBD were added to the solvent chloroform at a concentration of 15 mg/mL. The concentrations of lumophore emitters were implemented at 1% of the total weight. Chloroform solutions containing the host, and luminescent materials were prepared by stirring and then passed through 0.2 μm filters before spin-casting onto indium tin oxide (ITO) covered glass substrates. Before the application of the single organic layer, the substrates were cut into 1 in.^{2} pieces and cleaned using consecutive ultrasonic baths of acetone, methanol, and isopropyl alcohol. Radio frequency assisted plasma ashing for 2 min followed. The active layer was then prepared by spin casting at 1000 rpm for 60 s. Films were dried at 70−100 °C for 15 min in a nitrogen-filled glove box and then immediately transferred to a vacuum of about 5×10^{-7} Torr where the thermal evaporation of a Mg/Ag cathode at a 10:1 ratio was completed.

Results and Discussion

Design and Synthesis. The octakis(dimethylsilyloxy)-POSS (**1**) was chosen as the scaffold for this research because it is commercially available and is highly reactive with terminal alkene functional groups in the presence of a Pt catalyst. Virtually any substituent that can be modified to have a terminal alkene can be put on this POSS core, unless the steric hindrance prevents it from doing so. Monochromatic POSS emitter products (**POSS(B)$_8$**, **POSS(O)$_8$**, and **POSS(Y)$_8$**) were first synthesized with a 60, 61, and 47% yield, respectively (Scheme 1), to determine any effect of POSS on the emitters' physical properties, which will be discussed in a later section. The pure products can be easily collected after flash chromatography.

Next, the mixed POSS emitter products, such as **POSS(B)$_7$(O)$_1$**, **POSS(B)$_6$(O)$_2$**, or **POSS(B)$_5$(O)$_3$**, were synthesized (Scheme 2). Although a mixture of the different ratios of

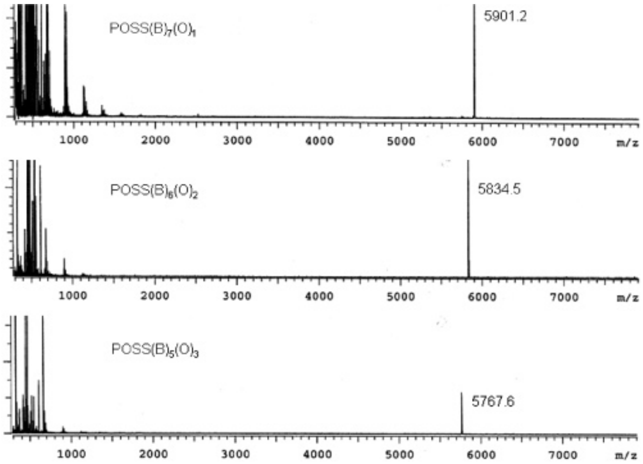


Figure 1. MALDI-TOF spectrum of **POSS(B)$_7$(O)$_1$**, **POSS(B)$_6$(O)$_2$**, and **POSS(B)$_5$(O)$_3$**.

Table 1. Effects of Mixed POSS Emitter Reaction Stoichiometry on Yields of Various POSS Products

reaction molar ratio			recovered yield %		
1	**2**	**3**	**POSS(B)$_7$(O)$_1$**	**POSS(B)$_6$(O)$_2$**	**POSS(B)$_5$(O)$_3$**
1	8	1.2	33	13	7
1	8	1.5	26	18	9
1	8	2.0	18	24	9

emitters substituted on POSS were produced, statistically, due to the nature of the nonselective reaction, it is controllable to a certain degree to produce one major product (in the case of this paper, **POSS(B)$_7$(O)$_1$)** by stepwise addition and by stoichiometric control of the reaction. Several mixed POSS emitter reactions were carried out, and the stoichiometry was varied each time by changing the molar ratio of) to find the effect on the final yield of the various POSS products. Although **POSS(B)$_7$(O)$_1$** was our desired major product, these experiments represent only a proof of principal that the major product can be varied by the stoichiometry of the reaction and do not represent a complete optimization of any one product. The results of these experiments can be seen in Table 1.

These various POSS products are then easily separable from each other by column chromatography, performed similarly as small molecule purification, to obtain monodisperse, pure products as shown by MALDI-TOF mass spectrum data (Figure 1) and elemental analysis (see Experimental Procedures). We believe this method can be used to create POSS materials with a mixed functionality in any desired ratio, assuming that the moieties attached to POSS have significant differences in polarity allowing for separation by chromatographic methods. It is the hope of the authors that by utilizing this approach in designing emitter materials for OLED application, with a proper choice of existing chromophores and the ratio of their combinations, any visible color may be generated from a single molecule including white light. However, the authors acknowledge that the chromophores selected for this study prevented the realization to fully control emission color due to a strong energy transfer within these mixed POSS emitter materials.

Thermal Properties. Thermal stability of the emissive materials is one of the most important aspects to improve device lifetime and reliability. It is well-known that the incorporation of POSS into materials can improve their thermal stability.[17] By incorporation of the emitters on POSS, the decomposition temperature (T_d) is increased by an average of 53 °C in nitrogen and 57 °C in air for the monochromatic POSS compounds relative to the free emitters themselves (Table 2). The T_d for the mixed emitter POSS compounds are all above 400 °C in nitrogen and air. The glass transition temperature (T_g) is another important factor in determining an OLED material's stability and shelf lifetime. The T_g values for these emitter functionalized POSS materials are all above 90 °C as indicated in Table 2.

Table 2. T_d and T_g of Materials

material	$T_{d5\%}$ (°C)^b		
	in N_2^{a}	in air^a	T_g (°C)
2	392	372	
POSS(B)$_8$	448	425	92
3	376	350	
POSS(O)$_8$	424	409	105
4	342	329	
POSS(Y)$_8$	397	388	94
POSS(B)$_7$(O)$_1$	444	417	94
POSS(B)$_7$(Y)$_1$	443	402	92

[a] TGA was performed at a heating rate of 10 °C/min under nitrogen or air atmosphere. [b] Temperature at which 5 wt % loss has occurred.

Table 3. A_{max} and λ_{max} of 2−4 and Emitter Functionalized POSS Materials

	solution^a		solid film^b	
compound	A_{max} (nm)	λ_{max} (nm)^c	A_{max} (nm)	λ_{max} (nm)^c
2	372	450	376	456
3	470	612^d	478	619^d
4	461	574^e	469	619^e
POSS(B)$_8$	373	450	373	456
POSS(O)$_8$	466	612^d	476	621^d
POSS(Y)$_8$	462	580^e	472	616^e
POSS(B)$_7$(O)$_1$	372, 472	450, 610	375, 480	590
POSS(B)$_6$(O)$_2$	372, 472	450, 610	375, 480	601
POSS(B)$_5$(O)$_3$	372, 472	610	375, 480	606
POSS(B)$_7$(Y)$_1$	372, 474	450, 580	375, 475	577

[a] Solvent = CH_2Cl_2. [b] Neat films spin cast from cyclopentanone on glass substrates. [c] Excitation wavelength = 370 nm unless otherwise noted. [d] Excitation wavelength = 470 nm. [e] Excitation wavelength = 460 nm.

Photophysical Properties. The monochromatic POSS emitters (**POSS(B)$_8$**, **POSS(O)$_8$**, and **POSS(Y)$_8$**) all have similar absorbance and emission spectra as their free emitter counterparts **2**, **3**, and **4** respectively, both in solution and in thin films (Table 3). The incorporation of the POSS core does not affect the color of the attached emitters.

However, there is a large difference in the spectra of the functionalized POSS materials containing more than one moiety of emitter. The blue emitter's emission spectrum shows a large degree of overlap with the orange (and yellow) emitter's absorption spectrum, indicating a significant potential for Förster energy transfer. In solution, the emission in the orange visible region (610 nm) dominates the PL spectra of the **POSS(B)$_7$(O)$_1$** material due to a strong intramolecular energy transfer from the blue emitter to the orange emitter, even though there is a 7:1 molar ratio of the blue emitter to the orange emitter on the molecule. To further study the effects of the covalent attachment of the emitters to POSS, a 1:7:1 molar ratio of **1**, **2**, and **3**, respectively, was mixed in dichloromethane to match the individual component concentration of the **POSS(B)$_7$(O)$_1$** material. The

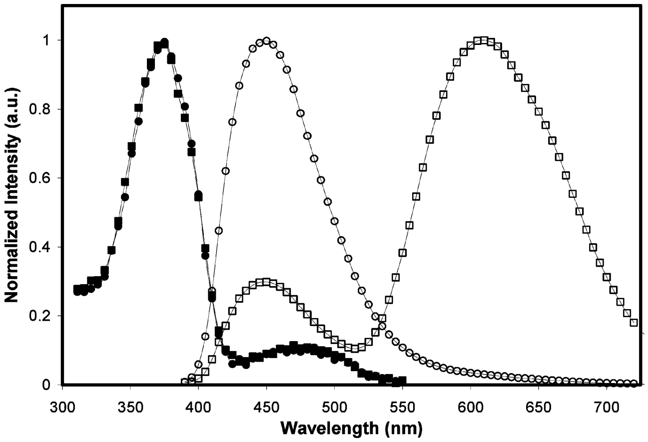


Figure 2. Normalized absorption (●) and PL (○) of **1**−**3** in a 1:7:1 molar ratio, respectively (1×10^{-7} M with respect to **1**), in a dichloromethane solution. Normalized absorption (■) and PL (□) of **POSS(B)$_7$(O)$_1$** (1×10^{-7} M) in a dichloromethane solution. Excitation wavelength is 370 nm.

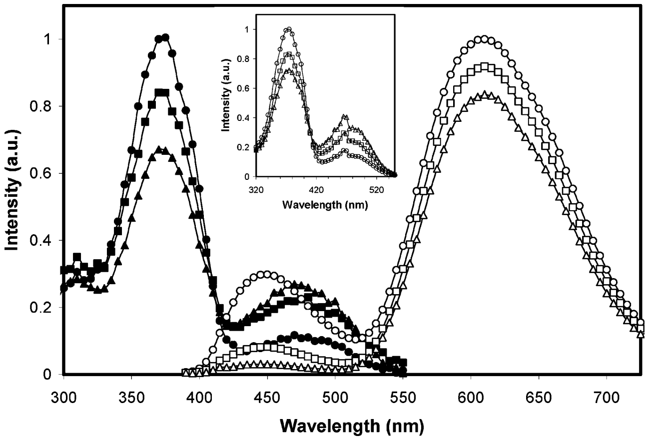


Figure 3. Absorption of **POSS(B)$_7$(O)$_1$** (●), **POSS(B)$_6$(O)$_2$** (■), and **POSS(B)$_5$(O)$_3$** (▲) and PL (excitation = 370 nm) of **POSS(B)$_7$(O)$_1$** (○), **POSS(B)$_6$(O)$_2$** (□), and **POSS(B)$_5$(O)$_3$** (△) in a dichloromethane solution (1×10^{-7} M). Inset: excitation spectra monitored at 610 nm.

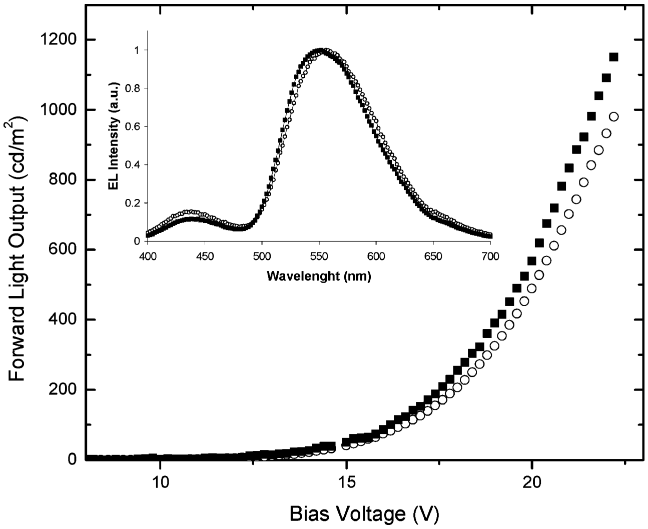


Figure 4. Voltage−luminance characteristics of OLED device with 1 wt % doped **POSS(B)$_7$(O)$_1$** (○) and **POSS(B)$_7$(Y)$_1$** (■). Inset: typical EL spectra of **POSS(B)$_7$(O)$_1$** and **POSS(B)$_7$(Y)$_1$** OLED devices.

absorption spectrum of the mixed system was identical to **POSS(B)$_7$(O)$_1$**. However, when excited at 370 nm, the emission spectrum of the mixed system does not reveal the orange peak (612 nm) nor the extent of quenching of the blue emission as seen in the **POSS(B)$_7$(O)$_1$** spectrum (Figure 2). Energy transfer is proportional to the molecular distance of the emitters involved. The distance between the blue emitters and the orange emitter is relatively constant on **POSS(B)$_7$(O)$_1$** due to the covalent bond between the dyes and POSS. This distance is relatively fixed regardless of the overall concentration in solution, and thus, energy transfer effects can still be seen even in dilute concentrations. No blue emission is seen in neat films of **POSS(B)$_7$(O)$_1$** or in the mixed free dye system due to strong intermolecular energy transfer in the solid state.

Upon comparison of the photophysical properties of the **POSS(B)$_7$(O)$_1$**, **POSS(B)$_6$(O)$_2$**, and **POSS(B)$_5$(O)$_3$** materials, further evidence of the energy transfer present in these POSS emitters can be obtained (Figure 3). As expected, the intensity of the absorption peaks of the blue emitter (370 nm) and the orange emitter (470 nm) correspond to the number of the blue and orange emitters present on the POSS core. The **POSS(B)$_7$(O)$_1$** material shows the most intense blue (450 nm) and orange (610 nm) emission when excited at 370 nm (excitation of the blue emitter). The excitation spectrum reveals that in all three mixed emitter POSS materials, the orange emission is most intense when excited at 370 nm, and these materials show much less orange emission and no evidence of blue (450 nm) emission when the orange emitter is directly excited at 470 nm.

EL data were collected for two OLED structures, one implementing the mixed functionalized material **POSS(B)$_7$(O)$_1$** and the other utilizing **POSS(B)$_7$(Y)$_1$** (Figure 4). The simple structure of ITO (150 nm)/PVK/PBD/dopant (120 nm)/Mg/Ag (330 nm) was shown to provide encouraging operational values. In this case, devices having **POSS(B)$_7$(O)$_1$** as the dopant had a turn-on voltage around 10 V with very low brightness (<2 cd/m^2). A forward light output of 100 cd/m^2 was achieved at 16.5 V as well as a current density of 5.71 mA/cm^2. The luminous efficiency in this case is 1.8 cd/A, with a maximum external quantum efficiency of 0.54%. These devices have CIE coordinates of (0.40, 0.50). A similar performance can be seen for devices doped with **POSS(B)$_7$(Y)$_1$**, where the turn-on voltage is also around 10 V. A bias voltage of 16.2 V (with a corresponding current density of 4.75 mA/cm^2) is needed to achieve a forward light output of 100 cd/m^2. The luminous efficiency in this case is ca. 2.1 cd/A; the maximum external quantum efficiency for these devices is around 0.6%, with CIE color coordinates of (0.39, 0.53). Increasing the brightness and efficiencies of these devices could be accomplished by adding better electron and hole transporting layers and/or charge and exciton blocking layers, but these more complicated constructions are beyond the scope of this paper. By measuring the EL spectrum, the amount of emission contribution from each of the lumophore moieties can be investigated. As predicted by photoluminescence data, emission from the blue lumophore is minimal as compared to both the yellow and the orange emissions. In fact, devices having PVK−PBD without the dopants were made, and their EL was recorded and agreed with already known values of emissions with a peak at around 420−435 nm corresponding to the PVK−PBD exciplex. A device consisting of **POSS(B)$_8$** doped at 1 wt % in a PVK−PBD host showed a peak EL emission at 450 nm. Moreover, a single layer, single component **POSS(B)$_8$** device was also made and showed a peak emission around 470 nm. This red shift relative to the doped device can be explained based on aggregation effects in the solid. With a PVK emission peak at 410 nm, PBD is known to emit at a lower wavelength than PVK. Thus, we can attribute the band peaked around 435 nm to the PVK−PBD exciplex and to contributions from the diluted blue emitter on the **POSS(B)$_7$(O)$_1$** (or **POSS(B)$_7$(Y)$_1$**) material. However, the majority of the EL emission is centered around 555 nm, corresponding to emission from the orange (or yellow) emitter. This unbalanced emission is due to the efficient and almost complete energy transfer from the high energy singlet state of the blue lumophore to the lower energy singlet state of the orange or yellow lumophore. Adequate control of such energy transfer processes will be the key to designing a future single macromolecule with white light emission.

Conclusion

In conclusion, we have demonstrated the first steps of a synthetic approach toward a solution processable single molecule emitter capable of emitting multiple wavelengths. We were able to fix the ratio of the emitter moieties on POSS by adequate control of the stoichiometry and stepwise addition of the various emitters during the reaction and recovered monodisperse pure materials after simple flash chromatography purification. All POSS materials showed better thermal stability relative to their free emitter counterparts. It was found that the emission from the lower energy emitter (orange or yellow) dominated the photoluminescence spectrum for the POSS materials containing more than one moiety of emitter due to strong intramolecular energy transfer from the neighboring higher energy blue emitters on POSS. The high degree of energy transfer is due to the overlap between the blue emitter's emission band and the lower energy emitter's (orange or yellow) absorption band, as well as from the short intramolecular distance of the blue and orange (or yellow) emitters. These materials were also shown to provide bright emission at reasonable operating voltages when made into single layer devices. We are currently investigating methods of adjusting the energy transfer by changing the tether length between the POSS core and the emitters or to saturate it by adding more blue-emitting dyes. The results of these investigations will be presented in a future paper.

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