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Organic−Inorganic Hybrids Based on Pyrene Functionalized Octavinylsilsesquioxane Cores for Application in OLEDs

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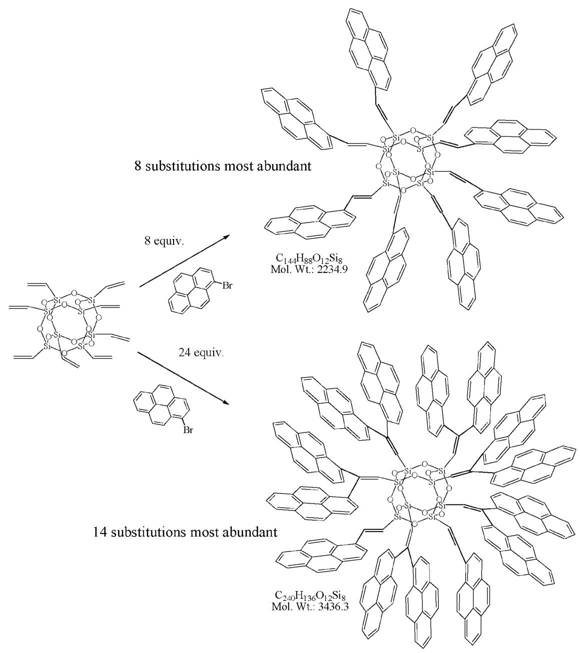
From a materials perspective, organic light emitting diodes (OLEDs) are primarily prepared from either small molecules or polymers.[1−4] Small molecules are advantageous in that they can be highly purified and vacuum deposited in multilayer stacks, both important for display lifetime and efficiency. However, vacuum deposition techniques require costly capital equipment, a limitation to practical display size and have significant problems in achieving full color displays at high volume using masking technologies.[5] Polymers are generally of lower purity than small molecules but can access larger display sizes and full color at much lower costs via solution-based deposition techniques.[6,7] Our interest is in the family of materials that combines the advantages of both small-molecule and polymer approaches to OLEDs—specifically silsesquioxane (SSQ) based hybrids. We have previously reported the effective use of hybrids based on silsesquioxane cores as hole transport materials in OLEDs.[8−10] We now extend this concept to prepare SSQ-based materials as the light emitting layers.[11−13] The materials contain a spherical "silica" core with a pyrene-functionalized emissive periphery. As opposed to most pyrene-based materials that are highly crystalline and non-emissive in the solid state, this material is completely amorphous and forms very photoluminescent powders and thin films. Furthermore, these materials offer many advantages for OLEDs including single step/high yield reactions, high glass-transition temperatures (T_g), low polydispersities, high solubility, and high purity via column chromatography.

Commercially available octavinylsilsesquioxane (OVS) was selected as the core SSQ material to react with varying feed amounts of 1-bromopyrene under Heck conditions, see Scheme 1. Unlike traditional Heck coupling reactions using styrene and methacrylate derivatives,[14] OVS is able to accommodate more than one addition across a single vinyl group.[10,15] Our intention was to exploit this unique property to observe how OVS cores with varying amounts of peripheral pyrene groups could affect the final materials and OLED properties. Reactions were carried out at 80 °C using initial 1-bromopyrene feed ratios of 8 and 24 equiv. Reactions were performed in toluene, using bis(tri-*t*-butyl-phosphine)palladium (0) $[Pd[P(tBu)_3]_2]$ (1.0 mol %) as catalyst and dicyclohexyl-methylamine as base/HBr scavenger.[16] On completion, the reaction mixture was precipitated into methanol to produce fine pale-yellow powders that were collected by filtration. The powders were dried, redissolved in minimal THF, filtered through a 1 μm filter into stirring methanol, and again collected by filtration. Final purification was achieved by column chromatography using dichloromethane/hexanes (3:1) to yield target materials in >80% yield.

Scheme 1 . Synthesis of Pyrene Substituted Octavinylsilsesquioxane (P8-OVS and P14-OVS) Using Heck Coupling



Matrix assisted laser desorption ionization-time-of-flight (MALDI-TOF) analysis using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix revealed substitution patterns of 4−10 (8 most abundant) and 12−16 (14 most abundant) for P8-OVS and P14-OVS, respectively. The MALDI spectrum for P14-OVS is shown in Figure 1.

Size exclusion chromatography (SEC) in THF for each material revealed single peaks with low polydispersity values of <1.05 suggesting no reactants, byproducts, or core breakdown during the reaction. As shown in Table 1, differential scanning calorimetry (DSC) reveals high-glass-transition temperatures (T_g) of 186 and

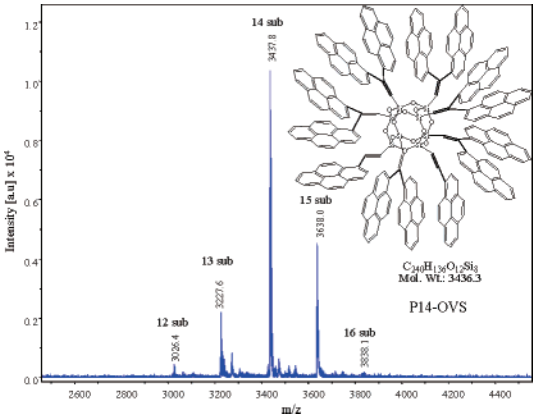


Figure 1. MALDI spectrum for P14-OVS.

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10.1021/ja070471m CCC: $37.00

Table 1. Optical and Thermal Properties for P8- and P14-OVS

compd	molecular weight	absorbance (nm)[a]	solution PL (nm)[a]	thin film PL (nm)	PLQE (%)[a]	T_g (°C)	T_d (°C)[b]	ceramic yield to SiO_2 (%)[c]	Average substitution[d]
P8-OVS	2234.9	289, 352	425	494	48	186	498	21.4	6.8
P14-OVS	3436.3	281, 349	431	506	55	226	496	14.3	13.6

[a] Photoluminescence (PL) and photoluminescent quantum efficiency (PLQE) measurements were done in toluene. Quinine sulfate used as a standard for PLQE measurements. [b] Decomposition temperature (T_d) was determined by thermal gravimetric analysis (TGA) at 5% mass loss, 10 °C/min in air. [c] Determined by TGA in air, 10 °C/min to 900 °C. [d] Average number of pyrene groups substituted onto octavinylsilsesquioxane (OVS) core based on TGA ceramic yield results.

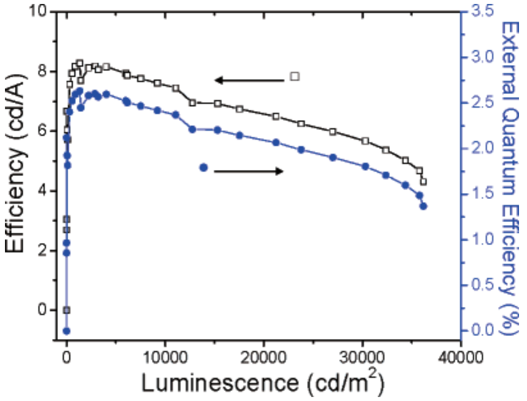

Figure 2. OLED device efficiency using P8-OVS as emitting layers in simple device structures [ITO/PEDOT (50 nm)/P8-OVS (55 nm)/TPBI (40 nm)/LiF (0.5 nm)/Ca (20 nm)/Ag (200 nm)].

Table 2. OLED Device Properties

emissive material	TOV[a]	cd/A (max)	EQE (%)[b]	cd/m^2 (max)	CIE
P8-OVS	3.1	8.28 @ 1330cd/m^2	2.63	36183 @ 17.5V	0.272, 0.567
P14-OVS	3.4	3.17 @ 775cd/m^2	1.15	11015 @ 15.0V	0.259, 0.475

[a] Turn-on voltage. [b] External quantum efficiency.

226 °C, respectively, for P8 and P14-OVS and no indication of melting or crystallization up to the decomposition point.

Thermal gravimetric analysis (TGA) in air reveals high thermal stability in excess of 495 °C and ceramic yields to SiO_2 of 21.4 and 14.3%, indicating an average substitution of 6.8 and 13.6, respectively, for P8- and P14-OVS. TGA in nitrogen shows T_d values in excess of 450 °C. The solution photoluminescence (PL) is red-shifted about 50 nm from molecular pyrene because of the extended conjugation through the vinyl−silane link. PL measurements show a 70-75 nm red shift between solution and thin films indicated some aggregation in the solid state may be occurring. Relatively high PL quantum efficiencies (PLQE) of 48 and 55% were calculated for P8- and P14-OVS indicating their possible utility for use in OLEDs.[17,18]

To demonstrate the potential of these SSQ hybrids in organic electronic applications, OLEDs were prepared using P8- and P14-OVS as emissive layers.[19] Devices for each material were prepared under identical conditions and results are shown in Figure 2 and Table 2. OLED devices with very similar efficiencies were prepared at both Arizona State University and IMRE Singapore to demonstrate reproducibility.

High brightness levels of 36183 cd/m^2 and external quantum and current efficiencies of 2.63% and 8.28 cd/A, respectively, can be reached using P8-OVS. To our knowledge, this exceeds the highest fluorescent efficiency achieved to date for a silsesquioxane based emitting layer by greater than 10×.[12] The lower device efficiencies for P14-OVS may result from the higher density of pyrene groups per unit volume that may lead to luminescent quenching in the solid state. In this regard, we next plan to test lower pyrene substituted hybrids, such as P3 and P6-OVS.

In conclusion, reported here is a new class of solution processable amorphous materials based on silsesquioxane cores with many attractive properties for application in organic light emitting diode (OLED) technology including ease of synthesis, high-glass-transition temperatures (T_g), good film-forming properties, low polydispersity, and high-purity via column chromatography. Preliminary unoptimized OLED external quantum and current efficiencies of 2.63% and 8.28 cd/A, respectively, demonstrate the utility of these materials as efficient emitters in OLEDs. Future work in this area will explore cores derivatized with other organic electronic functional groups for application in OLEDs, organic photovoltaics, and organic thin-film transistors.

Acknowledgment. We thank the Institute of Materials Research and Engineering (IMRE) and the Agency for Science, Technology and Research (A-STAR), Republic of Singapore for financial support. We thank Soon Yee Chang for help with OLED device fabrication.

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(19) In a typical experiment, ITO coated glass substrates were ultrasonically cleaned in sequential steps using acetone, methanol, and isopropanol. Poly(ethylenedioxythiophene)-polystyrene sulfonic acid (PEDOT-PSS, 2.5% in water) was spin coated, followed by baking at 120 °C under nitrogen for 30 min to provide a 50 nm layer. Active materials were spin-coated from toluene (P8-OVS) and ethyl benzoate (P14-OVS) 20mg/mL to yield a thickness of 55 nm. The substrates were then loaded into a vacuum chamber and a TPBI (40nm) layer was deposited followed by LiF (0.5nm), Ca (20nm), and Ag (200nm). TPBI as electron transport/hole blocking layer was important to achieve the high efficiencies.

JA070471M